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Doris C. Tuttle 1917 /25
Northrop House

○ ELEMENTARY
QUALITATIVE ANALYSIS

A LABORATORY GUIDE

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FIRST EDITION

FIRST THOUSAND

NEW YORK

JOHN WILEY & SONS, Inc.
London: CHAPMAN & HALL, Limited

1916

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BY

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PREFACE

THIS manual is offered as a laboratory guide for students of qualitative analysis who have had a year's work in general chemistry. It is the outgrowth of several years' experience with students registered in the varied courses of a university curriculum. The aim in the preparation of the book has been to systematize the work as much as possible, yet to avoid encouraging " rule of thumb " work in the laboratory.

Our viewpoint has been to give a sufficient number of well-organized characteristic reactions accompanied by appropriate questions to stimulate and encourage analytical thinking. The attempt is made to bring out the value of differential behavior toward reagents early so that the student has at the commencement of his qualitative study an idea of the ultimate application of the reactions.

We do not deem the study of the reactions used in the schemes followed in the systematic procedure for the analysis of unknowns sufficient ,to give the student a grasp of qualitative analysis. The use of analytical questions bearing on the reactions studied has an inestimable value in the student's analytical training and greatly broadens his knowledge of the chemistry of the metals.

In the outline for analysis the effort has been made to avoid asking impossibilities of the student, such as

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requiring a student to perform a separation containing interfering substances unless those substances have been identified and removed preceding the test in which the interference comes.

Several new departures from the usual scheme of analysis are followed, chief among these being a new scheme for the detection of the acids. The first group of acids is somewhat analogous to that given in Bailey & Cady's Qualitative Analysis. A systematic arrangement of this kind greatly shortens the time necessary for. the analysis of the acids and furnishes a nucleus around which the student can associate his work.

Whether the bases or acids should be tested for first in the course of analysis is a question which can be answered from two viewpoints. If the bases are tested for first the tests for the acids may be simplified in many cases and if the acids are analyzed for first then the procedure for the bases can usually be greatly abbreviated. Inasmuch as the detection of the acids requires much less time than that of the bases in the ordinary analysis for the common elements and likewise as the elimination of the bases saves many more steps in the systematic analysis we recommend the detection of the acids first.

The type headings for the preliminary tests are the reagents rather than the elements, as it is found that students more easily associate the reactions of this kind in a comparative way and the work progresses more rapidly in the laboratory, thus increasing efficiency. For a short course in the subject only the preliminary reactions with heavy type headings need be performed, while for a longer course all may be included.

Several discrepancies between the observed facts and the ionic theory as generally accepted have been made evident during the last few years by physicochemical meas-

urements. It is hoped that the theory will be adjusted
to the facts observed and not be thrown out regardless
of the good points possessed by it. The difficulty of ad-
justment and reconciliation of freezing or boiling points
with ionization in concentrated and dilute solutions does
not seem to be sufficient to cause the theory to be dis-
regarded. Within a few years a more uniform general
conception of the exact conditions will be available.

In the compilation of this manual many of the older
works and chemical periodicals have been consulted.
Space will not allow individual reference to all the
sources of the material utilized.

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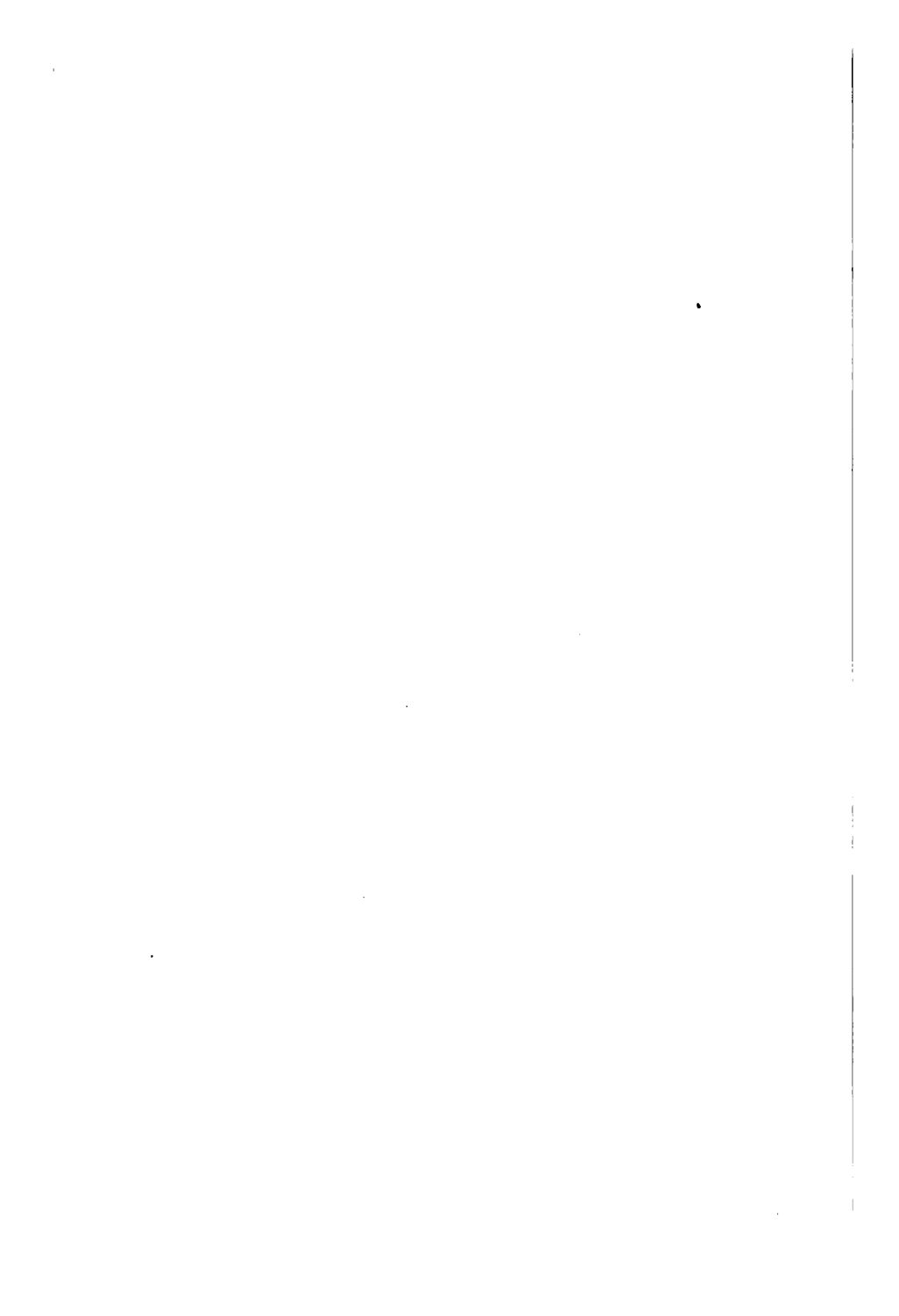
CHAPTER I

GENERAL DEFINITIONS AND PRINCIPLES OF QUAL-
ITATIVE ANALYSIS

Analytical chemistry is arbitrarily divided into two subjects of study each closely connected and interwoven with the other—*qualitative* analysis and *quantitative* analysis.

Qualitative Analysis is that branch of chemistry which deals with the *detection* (or quality) of the various substances, either alone or in the presence of others. Characteristic properties, as the physical nature and color of precipitates, solubility, color changes in solution, flame coloration, spectra, action on heating before the blowpipe flame, etc. are utilized in the processes of analysis.

Quantitative analysis deals with the determination of the *quantity* of any particular element or group of elements in the unknown being analyzed.

The subject of qualitative analysis being a very broad one can not be covered exhaustively in an elementary manual, hence only the common elements and compounds are considered. For a more comprehensive treatise on the subject the student is referred to the larger works of Fresenius, Prescott and Johnson, or Treadwell.

Browning's " Introduction to the Rarer Elements " is
an interesting brief book covering its particular field.
Information concerning the large field of carbon com-
pounds can be readily obtained from any standard text
on Organic Chemistry as Cohen, Holleman or Gatter-
mann.

Substances used to bring about chemical reaction are
called *reagents*. Reaction may be between gases, liquids,
solutions, solids, or any mixture of these. Solids react
with difficulty, heat usually facilitating reaction. Solu-
tions generally react readily and a study of the deport-
ment of various substances in solution is of the utmost
importance.

When two substances react in solution forming a
solid, *precipitation* is said to occur. When one substance
dissolves in another the one present in the smaller quan-
tity is generally called the *solute* and the other the *sol-
vent*. Frequently reaction between solutes varies consid-
erably with the solvent used. Magnesium will not be
precipitated by $(NH_4)_2CO_3$ from dilute aqueous solu-
tions containing NH_4Cl, but the addition of alcohol
changing the nature of the solvent causes the precipita-
tion of the magnesium.

A solid when brought into contact with a liquid in
which it is soluble passes into solution and the amount
of substance in solution increases if there is enough
solid until the concentration of the solute in the solvent
reaches a definite value independent of the amount of
solid present. Equilibrium is established and the solu-
tion is *saturated*. The condition of saturation of ordinary
solid substances depends upon three factors chiefly, the
solute, the solvent and the temperature; so that in con-
sidering the solubility of a substance it is necessary to
take into account not only the amount of dissolved sub-

stance but also the character of the solid which is in equilibrium with the solution and the temperature at which the solution is made. The amount of substance dissolved may either increase or decrease with a rise of temperature. The time element enters and varies with the state of subdivision of the substances. Agitation by shaking or stirring hastens saturation. In the case of a gas another factor, the pressure, is especially important.

If a saturated solution is cooled below the temperature of saturation with none of the solid substance which it contains present frequently no precipitation takes place and the liquid remains clear. Such a solution is said to be *supersaturated.* Should a crystal of the solid be then added, the solution vigorously agitated, or both, precipitation of the solid occurs until equilibrium is reached and the solution now becomes saturated at the lower temperature. Warming the solution causes it to become *unsaturated* and more solid can go into solution, again forming a saturated state. Similar states of unsaturation, saturation, and supersaturation can be obtained with gases in liquids and liquids in liquids.

In general we may have solid matter existing in the crystalline or amorphous state. Crystalline substances are regular in shape, have varied hardness, refrangibility, elasticity, tenacity, light absorbing powers, etc., in different directions. Amorphous substances, however, have no regularity of form and lack the varied properties ascribed to crystalline bodies. The properties are the same regardless of direction. Calcium carbonate and ice (snowflakes) are examples of crystals; glass and opal represent the amorphous class. When $(NH_4)_2CO_3$ is added to an ammoniacal solution containing calcium, crystalline $CaCO_3$ precipitates. However, when HCl is added to a solution of sodium silicate (water-glass)

silicic acid precipitates in the form of a gelatinous mass if the solution is concentrated. If not concentrated no precipitate may form or at most a cloudiness appears throughout the solution. If filtration is attempted no precipitate may be collected on the filter or a considerable amount may be collected on the filter in the form of an amorphous, jelly-like mass depending upon circumstances. Only vigorous agitation of the solution, adding some salt, boiling, evaporating to dryness, heating and again extracting with water or some such similar treatment will force the silicic acid from solution. Another example, suppose silver nitrate is added gradually to a solution of potassium chloride. Silver chloride precipitates, but the solution remains cloudy. Only with vigorous agitation of the solution, allowing the solution to stand several hours, heating, adding some other salt, or still better by the addition of an excess of silver nitrate, can the solution be forced to become clear, thus precipitating the AgCl in a form to be easily filtered. If we add ammonia to a very dilute solution of ferric salt no definite solid is formed but an opalescence is visible. If the iron solution is still weaker the solution may be almost clear. Boiling this solution, however, causes the iron hydroxide to coagulate and precipitate. Such states of matter are said to be colloidal. The soluble variety is called *hydrosol* (hydro from water—sol from soluble) and the insoluble variety *hydrogel* (-gel from gelatinous).

The action of acids, bases and nearly all salts in water solution is explained by the supposition that the molecules *dissociate* into component parts carrying charges of electricity. These parts are called *ions*. In the case of HCl, the ions are H, called the cation, and Cl, called the anion. We call the H ion the cation because when an electric current is passed through a solution of HCl,

the H goes to the negative electrode or cathode. The Cl ion is called the anion because under the same conditions it goes to the positive electrode or anode. The usual designation for the ions is the symbol or formula of its substance with a small plus or minus sign to indicate the amount of the electric charge each ion carries. Plus signs are used for cations because if these go to negative terminals they must be positively charged and negative signs for anions because they are attracted to positive terminals. The unit amount of electricity indicated by one plus or minus sign is that carried by an ion of a univalent element. H, Na, K ions are typical ions carrying one positive charge of electricity each and they are indicated by the symbols H^+, Na^+, K^+. Cl, Br, NO_3, CN ions are typical ions carrying one negative charge of electricity each, and these are indicated by the symbols or formulas Cl^-, Br^-, NO_3^-, CN^-. When a current of electricity is passed through a solution containing ions, the ions move to the oppositely charged terminal at which their electrical charge is neutralized and the ions then manifest themselves either in familiar forms that we know or in reactions characteristic of the substance without its electrical charge. For instance, when the H ions reach the negative terminal, they lose their positive charge and molecular H_2 will rise from the terminal and may be collected. Cl ions will have their negative charges neutralized when they reach the positive terminal and if that terminal happens to be carbon upon which nascent Cl has little action the Cl will rise from the terminal as molecular Cl_2. Na or K ions will have their positive charges neutralized when they reach the negative terminal, just as do H ions, but in these cases, the Na or K manifests itself by promptly decomposing some of the water of the solution, giving NaOH or KOH and

setting free H_2. It can easily be shown that an alkaline solution is formed at the negative terminal when an electric current is passed through sodium salt solutions if the negative terminal be placed in a porous cup. It is a simple matter to determine the amount of electricity required to liberate a gram atom (see page 12) of H. It is an equally simple matter to determine the amount of electricity required to liberate a gram atom of Cl, Br, Na, K. The amount of electricity required in each of these cases is the same. It is further capable of experimental proof that it requires twice this amount of electricity to precipitate a gram atom of Zn, Cd, ferrous Fe and that three times this amount of electricity is required to precipitate a gram atom of ferric Fe. By the same sort of electrical measurements it is found that the SO_4 group carries twice the negative electrical charge that the Cl ion does, and the PO_4 group three times that charge. The ions then of these substances are indicated thus: Zn^{++}, Cd^{++}, Fe^{++}, Fe^{+++}, SO_4^{--}, PO_4^{---}. The undissociated molecule of the substance is, of course, electrically neutral; consequently the number of positive charges borne by the cation or cations must be equal to the number of negative charges of the anion or anions. For example, when $FeSO_4$ dissociates the charges borne by the ions are two positive for the Fe and two negative for the SO_4. When HNa_2PO_4 is totally dissociated there is one positive charge for the H, two for the two Na's and these are offset by the three negative charges of the PO_4.

Nearly all substances of the three classes named above are assumed to separate in water solution into ions to a greater or less extent. As rapidly as the ions are formed they have a tendency to recombine and form the molecular substances again, hence there is a constant

readjustment or change. Suppose we have a solution of NaCl. Now if the solution is quite concentrated a large amount of the salt exists in the molecular condition, but considerable is *dissociated* into ions. As the solution is diluted the number of molecules present becomes less and less until in extremely dilute solutions the NaCl can be assumed to be almost completely ionized into Na^+ and Cl^-.

The ionization usually increases with dilution and decreases with concentration. This principle applies to all acids, bases and salts in solution. Let it be clearly understood that a current of electricity is not necessary for ionization, but the ions furnish the means of transmitting electricity when a current is passed through solutions containing them.

The student should keep the proper adjustment between *fact* and *theory*. We know that certain substances can be added to others and cause a reaction. That is *fact*. If for the purpose of definition we call certain particles that react *ions*, that is *theory*. The following consideration of the ions is entirely theoretical and we urge the student not to consider it otherwise. To say that an ion as a material particle exists in a solution is not necessarily correct, yet we can assume a charged particle called an ion in solution for purposes of explanation and classification of chemical facts.

The process of ion formation from molecular substances is called **Electrolytic Dissociation** or **Ionization.** Substances whose solutions are capable of conducting electricity are called **electrolytes** and the phenomenon of electric conduction in such solutions is called **electrolysis.**

Electrolytes as $CuSO_4$, Na_3PO_4, $AgNO_3$ in aqueous solution then undergo ionization, furnishing the ions Cu^{++},

$Na^+ + Na^+ + Na^+$, Ag^+ and SO_4^{--}, PO_4^{---} and NO_3^-. Then H_2SO_4 and all soluble sulphates will give SO_4^{--} ions in solution, Ba $(OH)_2$ and all soluble barium salts will give Ba^{++} ions in solution, hence qualitative analysis for the most part can be assumed to consist of the detection of the various cations and anions in solution. If a solution containing a soluble sulphate be added to a solution containing a soluble compound of barium the SO_4 ion can be assumed to combine with the Ba ion and solid $BaSO_4$ results. Likewise any compound in solution furnishing Ag ions will cause solid AgCl to form when added to any solution containing Cl ions. These two reactions constitute tests for the presence of barium and chlorides. The entire structure of analytical chemistry is built up on the fact that under manifold conditions the same identical compounds result, regardless of the source of the various ions reacting. The theory explains satisfactorily why a precipitate is not obtained when sodium or potassium chlorate in solutions of ordinary concentration are treated with silver nitrate solutions. The precipitation of silver chloride is a test for chloride ion, and chlorate solutions contain the ClO_3 ion, not the Cl ion. Not only that but as pointed out by Ostwald and carried out by others many physical properties can be traced to the presence of the ions. Hence appears the characteristic absorption spectrum of MnO_4^- in solution, and the emission spectra of the alkalies. Solutions containing Cu^{++} ions are greenish-blue, Fe^{++} greenish, CrO_4^{--} yellow, etc. Further, all ions present in colorless solutions have no color of their own, as H^+, K^+, Ba^{++}, Ca^{++}, Al^{+++}, F^-, Br^-, Cl^-, I^-, SO_4^{--}, NO_3^-, etc. Frequently the color can give interesting information in regard to the constituion of inorganic compounds. $K_4Fe(CN)_6$ does not possess the green

color of the Fe^{++} ion, but is yellow instead, hence must contain the iron in some other form, which is the complex ion $Fe(CN)_4^{----}$. When ammonia is added to a solution of a copper salt the color becomes a deep blue due to the change from Cu^{++} ion to $Cu(NH_3)_4^{++}$ ion. This solution can be decolorized by the addition of KCN forming the ion $Cu(CN)_2^-$.

All substances which furnish H^+ ions available for reaction are called *acids* (except acid salts). Substances which furnish $(OH)^-$ ions available for reaction are called *bases*. HCl, $HC_2H_3O_2$, H_2SO_4, ionizing into H^+ and Cl^-, H^+ and $C_2H_3O_2^-$, H^++H^+ and SO_4^{--} are types of acids. There is a great variation in the amount of dissociation for acids of the same molecular concentration. When .1 gram molecular (see page 12) amounts per liter are compared 90 per cent of HNO_3, HCl, HBr, HI, etc., are dissociated; of H_2SO_4 60 per cent; $HC_2H_3O_2$ 1.5 per cent; H_2CO_3 .2 per cent; H_2S .1 per cent; H_3BO_3 .01 per cent. The strength of the acid is measured by its capacity to furnish H ions, hence HNO_3 is stronger than H_2SO_4, much stronger than $HC_2H_3O_2$ and many times stronger than H_3BO_3. Na(OH), Ba(OH)$_2$, Sr(OH)$_2$, giving Na^+ and $(OH)^-$, Ba^{++} and $(OH)^-+(OH)^-$, Sr^{++} and $(OH)^-+(OH)^-$ ions are examples of bases. The strength of the base is dependent on the degree of dissociation or in other words the percentage ionization of the hydroxide. .1 molar (i.e. .1 gram molecular) solutions of NaOH and KOH are 90 per cent dissociated; Ba(OH)$_2$ 75 per cent; and NH_4OH 1.5 per cent.

In all cases of dissociation the number of unit charges of electricity carried by the cation or cations and the anion or anions resulting from ionization of a compound or compounds must be equal. When an acid reacts with a base the H^+ combines with the $(OH)^-$ forming H_2O.

This process is called *neutralization*. The other cation unites with the other anion and forms a substance called *a salt*.*

$$2Na(OH) + H_2SO_4 = Na_2SO_4 + 2H_2O, \text{ or}$$

$$2Na^+(OH)^- + H_2^{++}SO_4^{--} = Na_2^{++}SO_4^{--} + 2H^+OH^-.$$
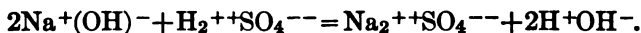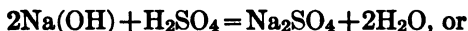
An acid containing one replaceable H^+ in the molecule is called *monobasic*, if more, *polybasic*, or specifically *di-*, *tri-*, and *tetrabasic*. Examples of each in order are

$$H^+Cl^-, \ H_2^{++}SO_4^{--}, \ H_3^{+++}PO_4^{---}, \text{ and}$$

$$H_4^{++++}Fe(CN)_6^{----}.$$
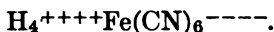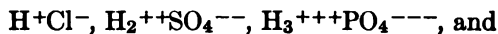
In addition to the *normal salts* having all their H^+ replaced by a base (Na_2SO_4), we have a different type which has only part of the H^+ replaced. This class is designated as *acid salts*, e.g., $NaHSO_4$, $KHCO_3$, $Ca(HCO_3)_2$. Similarly a base may have part of its hydroxyl unreplaced by other anions leaving a *basic salt* instead of a normal one which has all of the hydroxyl substituted. $Zn(OH)_2xZnCO_3$, $Fe(OH)_2C_2H_3O_2$, $Bi(OH)_2Cl$, etc. are examples of this class. Formulas for basic salts are often indicated by combination between one or more molecules of the base with one or more of the normal salt, thus

* Certain hydroxides as $Zn(OH)_2$ and $Pb(OH)_2$ may be considered either as bases or acids depending upon what reactions are involved. They may act as feeble bases furnishing OH ions neutralizing an acid forming salts or they may act as feeble acids furnishing H ions neutralizing a base. As acids they would be written H_2ZnO_2 and H_2PbO_2 reacting with NaOH forming soluble Na_2ZnO_2 and Na_2PbO_2. As bases they can dissolve in HNO_3 forming soluble $Zn(NO_3)_2$ and $Pb(NO_3)_2$. Such substances are called "amphoteric," capable of acting as either a base or an acid.

$Cu(OH)_2 \cdot CuSO_4$ or $Cu_2(OH)_2SO_4$ and for the acid salt frequently a similar combination between acid and normal salt, thus $CaCO_3 \cdot H_2CO_3$ or $Ca(HCO_3)_2$.

The simplest inorganic acids are the binary acids, which contain no oxygen, but consist of one element combined with H (HCl, H_2S). In nomenclature the termination -*ic* added to the names of the two elements or some obvious contraction of them is applied to the acids and -*ide* to the salts of the same. The latter suffix is used also to designate all binary compounds as the oxides, nitrides, phosphides, sulphides. One element often forms several oxygen acids, -*ic* and -*ous* being the terminations used for the common acids representing the higher and lower valences respectively, and -*ate* and -*ite* designating the corresponding salts. *Hypo*+ is used as prefix with -*ous* in naming the acids of still less oxygen content and *per*+ with -*ic* to name those containing more oxygen; the corresponding salts are called the *hypo*+-*ites* and the *per*+-*ates*. This nomenclature is well illustrated by the following series of acids and salts.

$HClO$ —hypo-chlorous acid.
$HClO_2$—chlorous acid.
$HClO_3$—chloric acid.
$HClO_4$—per-chloric acid.
$KClO$ —potassium hypo-chlorite.
$KClO_2$—potassium chlorite.
$KClO_3$—potassium chlorate.
$KClO_4$—potassium per-chlorate.

Bases may be oxides or hydroxides of the metals, including the alkalies, alkaline earths, lower oxides and hydroxides of the remaining metals, and the hydrides with their derivatives of certain non-metals, as NH_3, N_2H_4, NH_2OH, PH_3, etc.

Two or more salts sometimes combine in definite proportion to form a type of compounds called *double salts*, which are rather easily resolved into their constituent parts, e.g., $MgCl_2 \cdot 2NH_4Cl$. *Mixed salts* differ in that their constituents partly replace each other in equivalent proportions, e.g., $KNaCO_3$. Frequently a salt or double salt combines with a definite proportion of water of crystallization from aqueous solutions. These are called *hydrated salts*, e.g., $CuSO_4 \cdot 5H_2O$, $KCl \cdot MgCl_2 \cdot 6H_2O$. The water may be removed by heat. Some *effloresce*, give off water spontaneously when exposed to the air, e.g., $ZnSO_4 \cdot 7H_2O$.

In making solutions the atomic weight or molecular weight of the substance in solution is frequently taken in grams, hence the designation *gram atom* and *gram molecule*. Weights of various substances which correspond to their atomic or molecular weights are called *atomic* and *molecular quantities*, thus 39.1 grams, 137.4 grams, and 107.9 grams represent a gram atom each of potassium, barium, and silver, and 174 grams, 208 grams, and 170 grams represent a gram molecule each of potassium sulphate, barium chloride, and silver nitrate. A *normal solution* contains in each liter of solution a gram molecule of the substance divided by its hydrogen equivalent. Hence a normal solution of hydrochloric acid would contain $\frac{36.45}{1}$, of sulphuric $\frac{98}{2}$, of barium chloride $\frac{208}{2}$, of silver nitrate $\frac{170}{1}$, and phosphoric acid $\frac{98}{3}$ gm. per litre. Normal solutions are usually marked "N" or "n" solutions. $2N, 5N, .1N, .5N, \frac{n}{10}, \frac{n}{20}, \frac{n}{50}, \frac{n}{100}$ express proportions in terms of normality. $\frac{n}{10} HCl$ would contain 3.645 gm., $\frac{n}{20}$ 1.823 gm., and $\frac{n}{100}$ 0.3645 gm. of HCl per liter of solution. If a liter of .1N NaCl, containing 5.85 gm. of NaCl, is caused to react with a liter of .1N $AgNO_3$ containing 17 gm. of $AgNO_3$ the reaction

between the two salts goes to completion, leaving neither $AgNO_3$ nor $NaCl$ in excess. However, 14.35 gm. of $AgCl$ is precipitated and 8.5 gm. of $NaNO_3$ remains in solution. Likewise if a liter of .2N $NaOH$ be caused to react with a liter of .2N H_2SO_4 a neutral solution of Na_2SO_4 results.

In qualitative analysis the reactions chosen are either nonreversible or reactions which, under the conditions outlined, proceed largely in one direction only. However, most reactions are reversible and proceed to an equilibrium point at which we have not only the anticipated end products but some of the reacting substances as well. A brief study of the equilibrium law and of some of its applications is therefore desirable.

By a reversible reaction is meant one which can be made to proceed in one direction, forming new products, or backward, reforming the original reagents by altering the temperature, pressure or concentrations of one or more of the reagents or products. Those reactions which are not reversible are so by nature, as for instance the burning of magnesium in oxygen or the inversion of cane sugar. A change of the conditions causing either of these chemical changes hastens or retards the reaction but does not cause it to reverse itself.

The precipitation of CdS from $CdCl_2$ solution by H_2S is an excellent example of a reversible reaction and is expressed thus:

$$CdCl_2 + H_2S \rightleftarrows CdS + 2HCl.$$
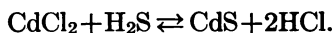
Now if we take a solution of cadmium chloride and add to it just the theoretical amount of hydrogen sulphide required to unite with the cadmium present, we shall obtain a precipitate of cadmium sulphide, but not all of the cadmium will be precipitated from the solution. The

hydrochloric acid as it forms has a tendency to dissolve cadmium sulphide, thus stopping the precipitation short of completion. In other words, an equilibrium has been established in the solution.

The equilibrium law is a more convenient way of considering the law of mass action enunciated by Guldberg and Waage in 1867, which states that the rate at which a reaction proceeds and the resulting amount of chemical change are proportional to the active masses of the reacting substances. Let us consider a general equation $A + B \rightleftharpoons C + D$. If a and b are the active masses of A and B respectively, expressed in fractions of gram molecular weights, and x the amount of A and B changed at any given time, the rate $= K \cdot a \cdot b$ when $x = 0$ at the beginning, but the rate $= K(a-x)(b-x)$ afterward, in which cases K is a constant. In the same equation if c and d are the active masses of C and D, then at the beginning the rate of the reverse action is $K' \cdot c \cdot d$ and $K'(c+x)(d+x)$ at any time afterward. $K' \cdot c \cdot d$ may be zero if none of the products of the reaction were there originally. As the reaction proceeds there must come a time when the rates of the forward reaction and the reversed reaction are equal and then we have $K(a-x)$ $(b-x) = K'(c+x)$ $(d+x)$ or $\dfrac{(a-x)\,(b-x)}{(c+x)\,(d+x)} = \dfrac{K'}{K}$. This is the condition which prevails when equilibrium is reached. It may be stated that at equilibrium the product of the molecular quantities of the reacting substances divided by the product of the molecular quantities of the products formed is a constant.

There are many applications of this equilibrium law in analytical chemistry, perhaps the most important for present purposes being those to various phases of ionization. Such phenomena as increasing the quantity of

precipitate by addition of a slight excess of a reagent and decreasing the strength of an acid by adding a substance containing a common ion are based mostly on the so-called solubility product.

A case of ionization will be considered. All such cases may be regarded as reversible reactions in which the molecules dissociate into ions and these combine again into molecules under given conditions of temperature and pressure until there is as much composition as decomposition and the system comes into equilibrium. For example NaCl dissociates, thus $NaCl \rightleftarrows Na^+ + Cl^-$. If c is the molecular concentration of NaCl, a the ionic concentration of Na^+ and b that of $Cl,^-$ then the " rate " of decomposition of $NaCl = Kc$, while the " rate " for the composition of the salt is $K'ab$. If these two values are equal then $K'ab = Kc$ or $\dfrac{ab}{c} = \dfrac{K}{K'} = a$ constant, which is called the ionization constant.

In considering why the quantities of difficultly soluble substances that can be precipitated from solution are increased by the addition of a slight excess of the reagent we make use of a special case of the ionization equation given above. When a substance is precipitated from solution it may often be proved and always assumed that there is left in solution all of the substance the liquid can keep in solution in the presence of the solid which is precipitated. In other words, a saturated solution of the precipitated substance is what we have. For the special case of the saturated solution the value of c in the equation $\dfrac{a \cdot b}{c} = K$ becomes constant and so may be incorporated with K, then $a \cdot b = Kc = K'$. Now a and b are the amounts of ions in the saturated solution and their product is known as the " solubility product." If this

product be disturbed by the addition of some substance in solution which contains one of the ions, thereby increasing a or b, b or a will be decreased and more undissociated molecules formed, in consequence of which more salt will be precipitated because the solution is already saturated with salt molecules. Consider the precipitation of lead sulphate and the matter of increasing the amount of lead sulphate precipitated by means of a slight excess of sulphuric acid or a sulphate in solution. In the saturated solution of lead sulphate left after making the precipitation we shall have lead ions and sulphate ions in such quantities that $a \cdot b =$ a constant, where a is the amount of lead ion and b the amount of sulphate ion. When sulphuric acid or a sulphate in solution is added, an excess of b is added. To preserve the truth of the equation $a \cdot b = K$ a must diminish. The only way this can happen is for more undissociated lead sulphate to be formed. But this means that lead sulphate must be precipitated, for the solution is saturated with respect to lead sulphate molecules or c of the equation we are considering.

In decreasing the strength of an acid in a solution by use of a substance containing a common ion we are doing the same thing as in the previous case, except that we do not start with a saturated solution. For any given acid, say acetic, under given conditions $\dfrac{a \cdot b}{c} = K$, when a and b are the concentrations of H and $C_2H_3O_2$ ions respectively and c that of undissociated $HC_2H_3O_2$. If we add $NaC_2H_3O_2$ or $NH_4C_2H_3O_2$ to the solution we largely increase b. If $\dfrac{a \cdot b}{c} = K$ is to hold, then a must decrease or c must increase and both of these happen, for if the concentration of H ion decreases more undissociated $HC_2H_3O_2$

molecules must be formed. This is well illustrated by the reaction of potassium iodate and potassium iodide in acetic acid solution. Potassium iodate and iodide do not react in neutral solution. However, the reaction can be caused to proceed rapidly with the liberation of iodine by the addition of the proper amount of acetic acid. If sodium acetate is added to the solution, the liberation of iodine, and consequently the entire reaction, can be prevented or stopped almost completely. The addition of the common ion $C_2H_3O_2{}^-$ (b) diminishes the H^+ ions (a) to such an extent that the reaction almost ceases entirely.

Let us consider the solubility of NaCl in water. NaCl is moderately soluble in water (36 parts per 100 parts water at 18° C.). However, if you make a saturated solution of salt and add strong HCl to it, NaCl precipitates at once. Thus we have lessened the solubility of NaCl by adding HCl. Potassium chlorate is much less soluble than sodium chlorate. Consequently when a saturated solution of sodium chlorate is added to a saturated solution of potassium chlorate some of the latter is precipitated at once. When concentrated nitric acid is added to a strong solution of silver nitrate the latter is thrown out instantly, inasmuch as it is the less soluble. The HCl added increases the quantity of chlorine ions, thus causing association of sodium and chlorine, forming molecular NaCl. Increase of ClO_3 and NO_3 ions respectively likewise brings about association, forming molecular $KClO_3$ and $AgNO_3$. Chlorine is common to both NaCl and HCl; ClO_3 is common to both $KClO_3$ and $NaClO_3$; NO_3 is common to $AgNO_3$ and HNO_3; hence each result enumerated is attributed to the " common ion effect."

The amount of any substance precipitated is dependent

upon the quantity of reacting substances involved. In case of the precipitation of NaCl by gaseous HCl, if only a small amount of HCl is added very little salt may precipitate. However, if a large amount of the acid is added the precipitation of the NaCl may be almost complete. Then the effect of any reaction is dependent upon the concentration of the reacting substances. This fact finds expression in the previously described *law of mass action. The speed or rate and likewise amount of any chemical change is proportional to the active mass of each substance engaged in the reaction.*

The mass of any chemical reagent is regulated to apply to the specific reaction desired. Some reactions, such as neutralization of acids and alkalies, go to completion with molecular quantities involved requiring no excess of reagent. Other reactions require a somewhat greater concentration of reagent to cause reactions (especially to make them go to completion), e.g., precipitation of antimony sulphide with hydrogen sulphide from acid solutions. The reduction of potassium dichromate by hydrochloric acid requires a still greater excess of reagent. Other reactions require a large excess of reagent in order to complete the reaction, e.g., the precipitation of phosphoric acid with ammonium molybdate, the solution of many natural sulphides in hydrochloric acid, etc. The amount of reagent is also regulated from another point of view. If the same solution is to be used for other tests, in general an unduly large excess of the reagent is to be avoided, especially if the reagent adds material which must be removed before making subsequent tests. Naturally the temperature, pressure, and the solvent are likewise determining factors.

Theoretically all solids are soluble in water, alcohol, acetone, etc. However, the solubility may be so slight

as to be negligible.   The terms " solubility " and " in-solubility " are purely relative, the meaning of the words being dependent upon the specific use.   Miscellaneously a solid is commonly said to be insoluble when the solubility is less than one part in five to seven hundred parts of solvent.   In many cases the insolubility is many times greater than this, yet in all cases there is always a solubility of the solid in the medium involved.   AgCl and BaSO$_4$ are among our most insoluble substances, yet even these are soluble to a slight extent.   .000016 gm. AgCl dissolves in 100 cc. of water at 18° C. and .000023 gm. BaSO$_4$ dissolves in the same volume of water at the same temperature.   However, they are much less soluble in water containing ions common to these compounds.

In selecting a reaction to be used to identify the presence of an element or radical by precipitation of an insoluble substance several points must be considered: (1) the compound to be formed must have a high degree of insolubility; (2) the volume of solution used must be correspondingly small; (3) the compound to be formed must be distinctive, i.e., other elements or radicals must not give a similar precipitate with the same solution when the test is applied.   If a test common to two or more elements or radicals is to be used for final identification of these elements or radicals, then other reactions must be used to separate the same before the reaction can be applied in each case.

The same logic holds for the identification by color change, by the flame color, heating with a blowpipe, etc. For final confirmation the proof must be distinctive.   If the identification is not distinctive, then the interferences must be removed or another test applied.

CHAPTER II

CHEMICAL REACTIONS AND EQUATIONS

THE term *reaction* is used to designate any chemical action involved. An *equation* is the mathematical expression of the reaction. A carbonate and hydrochloric acid will react and the reaction is expressed by an equation, thus $CaCO_3 + 2HCl = CaCl_2 + H_2O + \widetilde{CO_2}$. Gases are designated frequently by a wave line over the compound as $\widetilde{CO_2}$. Precipitates may be differentiated by a straight line beneath the compound, as $\underline{BaSO_4}$.

The simplest form of reaction is that of *decomposition* (separating process) which may be effected by such agencies as heat, light, electricity, for example, $CuCl_2 +$ current of electricity $= Cu + Cl_2$, $ZnCO_3 + heat = ZnO + CO_2$. Agencies like those mentioned above may affect *synthesis* (building up process), e.g., $Fe + S + heat = FeS$, $Sb + 3\ Cl = SbCl_3$. Two salts may react to give *double decomposition* as $2NH_4Cl + K_2SO_4 \rightleftarrows 2KCl + (NH_4)_2SO_4$, the double arrow indicating a reversible reaction. Such a reaction is frequently accompanied by precipitation of an insoluble compound, as $AgNO_3 + HCl = \underline{AgCl} + HNO_3$; or the escape of a volatile compound into the atmosphere, $MnS + H_2SO_4 = MnSO_4 + \widetilde{H_2S}$.

Some reactions are simply those of substitution, as $Zn + H_2SO_4 = ZnSO_4 + \widetilde{H_2}$, $2Al + 6NaOH = 2Al(ONa)_3 + \widetilde{3H_2}$.

Acids and bases react to form salts and water through the process called *neutralization*, $NaOH + HNO_3 = NaNO_3 + H_2O$.

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H_2SO_4 reacts on salts of volatile acids liberating the latter. $H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$.

CHEMICAL CHANGE THROUGH OXIDATION AND REDUCTION

Many reactions involve a chemical rearrangement of the constituent material, causing a readjustment of the oxygen within the system.   In these reactions the elements naturally go to their most stable conditions under the subjected treatment and the reactions are quite well-defined processes.   One shortly learns to distinguish certain compounds which strongly resist any effort to remove or receive any oxygen, while others lose or gain oxygen more or less readily; H_2O, CO_2, Fe_2O_3, K_2SO_4, SiO_2, etc., are very stable, while $KClO_3$, HgO, Ag_2O, PbO_2, $KMnO_4$, etc., lose oxygen with ease, and Na_2SO_3, $FeSO_4$, etc., have a great affinity for oxygen either directly or indirectly.

The process through which the oxygen leaves one compound to combine with another is called *oxidation* with respect to the substance *receiving oxygen* and *reduction* in reference to the material *losing* it, and the compounds effecting the changes are called *oxidizing* and *reducing* agents.

$$H_2SO_3 + H_3AsO_4 = H_2SO_4 + H_3AsO_3$$
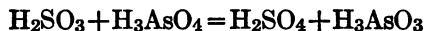
The sulphur in sulphurous acid is oxidized, forming sulphuric acid, and the arsenic in arsenic acid is reduced, forming arsenous acid.

When the valence of an element is raised or lowered it is said to be oxidized or reduced, as the equivalent of oxygen is always involved.   Example: $2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2$.   Iron is reduced, changing in valence from three to two, giving up one atom of chlorine, which is the equivalent of one-half an atom of oxygen.   The

tin changes in valence from two to four, hence is oxidized, combining with two atoms of chlorine, which are equivalent to one atom of oxygen in reaction.

There are three distinct methods of writing equations involving oxidation and reduction, called the " oxygen equivalent," " double oxide," and " bond " systems.

Oxygen Equivalent Method

In the first the number of oxygen atoms or their equivalent furnished by the oxidizing agent is expressed by one equation and the number of oxygen atoms or their equivalent used by the reducing agent is expressed by another. If a secondary reaction occurs involving the products formed above (as the action of an acid on an oxide), this reaction is expressed by an equation. Then the equations are added algebraically. Hence balancing an equation becomes a simple process of finding the least common multiples and greatest common divisors of the compounds on the left-hand side of the equality sign.

EXAMPLES. $SnCl_2 + FeCl_3 = ?$
(1) $FeCl_3 = FeCl_2 + Cl$
(2) $SnCl_2 + Cl_2 = SnCl_4$
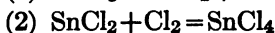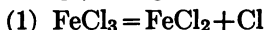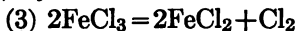
Multiply (1) by 2
(3) $2FeCl_3 = 2FeCl_2 + Cl_2$

Adding (2) and (3)
(4) $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2.$

$PbS + HNO_3 = ?$
(1) $2HNO_3 = H_2O + 2NO + 3O$
(2) $PbS + O = PbO + S$

Multiply (2) by 3
(3) $3PbS + 3O = 3PbO + 3S$

Secondary Reaction

(4) $PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O$

Multiply (4) by 3

(5) $3PbO + 6HNO_3 = 3Pb(NO_3)_2 + 3H_2O$

Add (1), (3) and (5)

$3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 4H_2O + 2NO + 3S.$
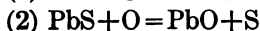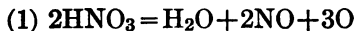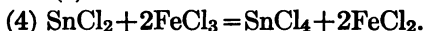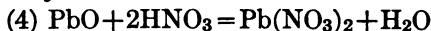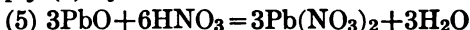
Final equation.

Double Oxide Method

In this method all the compounds entering into reaction that may be so written are expressed as their double oxides. The change of the number of oxygen atoms from the oxidizing to the reducing agents is then noted and the process of finding the least common multiples and common divisors is carried out as in the first method.

EXAMPLES: $CuS + HNO_3 = ?$

Expression of products of reaction

$CuS + HNO_3 = Cu(NO_3)_2 + H_2O + NO + S$ or

$CuS + H_2O \cdot N_2O_5 = CuO \cdot N_2O_5 + H_2O + N_2O_2 + S$
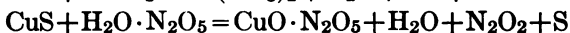
Nitric acid is written $H_2O \cdot N_2O_5$ because two atoms of N enter into N_2O_5.

The change from N_2O_5 to N_2O_2 is expressed $H_2O \cdot N_2O_5$ $= H_2O + N_2O_2 + 3O.$ \hfill (1)

The change from CuS to CuO is expressed $CuS + O$ $= CuO + S.$ \hfill (2)

Multiply by three to obtain common multiple, $3CuS + 3O = 3CuO + 3S.$ \hfill (3)

Oxide+acid, $CuO + H_2O \cdot N_2O_5 = CuO \cdot N_2O_5 + H_2O.$ (4)

Multiply by three to obtain common multiple

$$3CuO + 3H_2O \cdot N_2O_5 = 3CuO \cdot N_2O_5 + 3H_2O. \tag{5}$$

Add (1), (3) and (5)

$$3CuS + 4H_2O \cdot N_2O_5 = 3CuO \cdot N_2O_5 + N_2O_2 + 4H_2O + 3S.$$
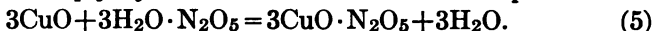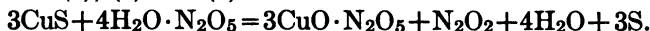
This final equation is then converted into the ordinary form:

$$3CuS + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O + 3S.$$

$$PbO_2 + H_2SO_4 + MnSO_4 = ?$$

Expression of products of reaction

$PbO_2 + H_2SO_4 + MnSO_4 = HMnO_4 + PbSO_4 + H_2O$ or
$PbO \cdot O + H_2O \cdot SO_3 + Mn_2O_2 \cdot 2SO_3 = H_2O \cdot Mn_2O_7 + PbO \cdot SO_3 + H_2O.$
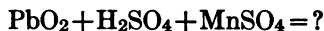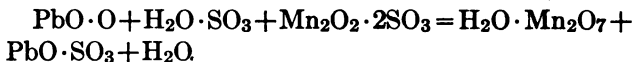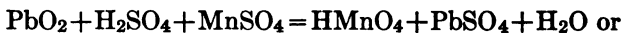
$MnSO_4$ is written $Mn_2O_2 \cdot 2SO_3$ because 2 atoms of Mn exist in $H_2O \cdot Mn_2O_7$.

The change from $PbO \cdot O$ to PbO is expressed $PbO \cdot O$

$$= PbO + O. \tag{1}$$

The change from Mn_2O_2 to $H_2O \cdot Mn_2O_7$ is expressed

$$Mn_2O_2 \cdot 2SO_3 + 3H_2O + 5O = H_2O \cdot Mn_2O_7 + 2H_2O \cdot SO_3. \tag{2}$$

Multiply (1) by 5 to obtain common multiple

$$5PbO \cdot O = 5PbO + 5O. \tag{3}$$

Oxide + acid $5PbO + 5H_2O \cdot SO_3 = 5PbO \cdot SO_3 + 5H_2O.$ (4)

Add (2), (3) and (4) $5PbO \cdot O + Mn_2O_2 \cdot 2SO_3 + 3H_2O \cdot SO_3 = H_2O \cdot Mn_2O_7 + 5PbO \cdot SO_3 + 2H_2O,$ or $5PbO_2 + 2MnSO_4 + 3H_2SO_4 = 2HMnO_4 + 5PbSO_4 + 2H_2O.$
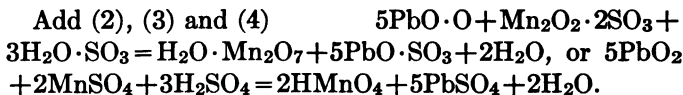
The Bond Method

In the so-called " bond method " the number of " bonds " or " valences " (on the basis of hydrogen hav-

ing the valence of one or one bond) gained or lost in a reaction is adjusted between the oxidizing and reducing agents by a mathematical process similar to the schemes given above. The bond change of the reducing element or elements is usually considered first and the bond change of the oxidized element or elements adjusted to counterbalance exactly the former. The coefficients of the other substances present can then be easily ascertained by addition or subtraction.

EXAMPLE. $FeSO_4 + KMnO_4 + H_2SO_4 = ?$

First express the products of reaction, thus—

$FeSO_4 + KMnO_4 + H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + H_2O.$
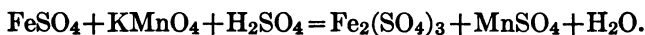
Next notice the " bond change " of each element. Since the number of positive bonds must exactly counterbalance the negative bonds in the same compound, we have the following changes to consider. In $FeSO_4$, the iron carries two bonds with the SO_4. But in $Fe_2(SO_4)_3$ the iron has three bonds or a gain of one bond for each atom considered, giving a gain of two bonds in the change of two molecules of ferrous to one molecule of ferric sulphate.

In $KMnO_4$, potassium has one, manganese seven and oxygen two bonds for each atom present or a total of eight bonds. Manganese in $MnSO_4$ has two bonds of union with the SO_4. Hence the change in the manganese is five bonds.

Adjusting the bonds on the basis of ten as multiple, ten atoms of iron gain ten bonds and two atoms of manganese lose ten bonds.

Hence $2KMnO_4$ will react with $10FeSO_4$. Completing the equation, taking sufficient H_2SO_4 to form sulphates of the bases present, we have $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$

The hydrogen and oxygen will always be present in the proper proportions to form water, as the reduction equals the oxidation.

Balance the following equations:

$Ag_2S + HNO_3 = AgNO_3 + NO + S + H_2O$

$CoCl_2 + KOH + Br = Co(OH)_3 + KBr + H_2O$

$K_2Cr_2O_7 + H_2S + HCl = CrCl_3 + KCl + H_2O + S$

$PbO_2 + H_2SO_4 + MnSO_4 = PbSO_4 + HMnO_4 + H_2O$

$C_2H_6O + HCl + K_2Cr_2O_7 = KCl + CrCl_3 + C_2H_4O + H_2O$

$NaCl + H_2SO_4 = Na_2SO_4 + HCl$

$KCl + MnO_2 + H_2SO_4 = K_2SO_4 + MnSO_4 + H_2O + Cl$

$H_2C_2O_4 + KMnO_4 + H_2SO_4$

$\qquad = K_2SO_4 + MnSO_4 + H_2O + CO_2$

$FeCl_3 + H_2S = FeCl_2 + HCl + S$

$H_2CrO_4 + KI + HCl = I + H_2O + CrCl_3 + KCl$

$Cu(NO_3)_2 + H_2S = CuS + H_2O + NO + S.$
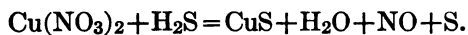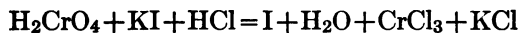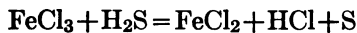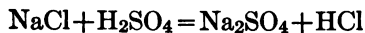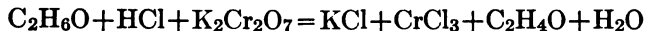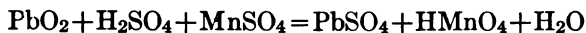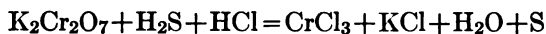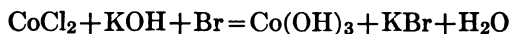
CHAPTER III

ANALYTICAL GROUPS

THE elements are grouped in qualitative analysis according to their analytical reactions. The elements or combination of elements acting as one element are divided into two main divisions, one of which contains the bases and the other the acids. These divisions are each subdivided into several groups.

The Bases

The separation of the bases into groups is founded essentially on the solubility of the various sulphides. The first two groups of metals give sulphides insoluble in moderately dilute hydrochloric or sulphuric acids (although the first group metals are precipitated by hydrochloric acid for convenience), the third group metals give sulphides insoluble in alkaline solutions and the fourth group sulphides are soluble in both acid and alkaline solutions.

The First or *Hydrochloric Acid Group* contains silver (Ag) and mercur*ous* mercury (Hg), with the valence of one and lead (Pb) with the valence of two. These elements are so classified because they are precipitated from slightly acid solutions by the addition of hydrochloric acid.

The Second or *Hydrogen Sulphide Group* contains mercur*ic* mercury (Hg), lead (Pb), copper (Cu), cadmium (Cd) and stan*nous* tin (Sn) with the valence of

two, bismuth (Bi), arsen*ous* arsenic (As) and antimon-*ous* antimony (Sb) with the valence of three, stann*ic* tin (Sn) with the valence of four, and arseni*c* arsenic (As) and antimoni*c* antimony (Sb) with the valence of five. This classification is possible because of the insolubility of the sulphides in dilute acid solution which contains an excess of hydrogen sulphide. (Lead occurs in both groups due to the slight solubility of the chloride in water. In many cases it will be found in analysis in both groups and again only in one, depending on the concentration and temperature of the lead solution preceding the addition of hydrochloric acid.)

The Third or *Ammonium Sulphide Group* contains nickel (Ni), cobalt (Co), ferrous iron (Fe), manganous manganese (Mn) and zinc (Zn) having the valence of two, chromium (Cr) and aluminum (Al) of the valence of three, and titanium (Ti) of the valence of four, due to the fact that they are precipitated from alkaline solutions by ammonium sulphide. Ferric is reduced to ferr*ous* iron, chrom*ates* to chrom*ic* salts, manган*ates*, permangan*ates* and manganic manganese to the manganous state, cobalt*ic* to the cobalt*ous* and nickel*ic* to the nickel*ous* state by H_2S and other reducing agents. By the use of appropriate oxidizing agents the valences of these elements may be changed from the lower to the higher.

The Fourth or *Ammonium Carbonate Group* contains calcium (Ca), strontium (Sr), barium (Ba), having the valence of two, which are precipitated by the reagent ammonium carbonate. Magnesium (Mg) with the valence of two, potassium (K), sodium (Na) and lithium (Li) with the valence of one, are not precipitated by means of that reagent but are included in this group for the convenience of the analyst.

The Acids

The acids are divided into three groups based essentially on the solubility of their silver salts. The first group of acids gives silver salts insoluble in dilute nitric acid solutions, the second group contains those acids (not including those of the first group) giving silver salts insoluble in neutral or faintly acid solutions and the third group contains acids giving silver salts not sufficiently insoluble to be classed in the two previous groups and the acids which must be tested for directly in the original material or an alkaline solution prepared from the original.

The First or *Acid Silver Group* includes hydrochloric (HCl), hydrobromic (HBr), hydriodic (HI), iodic (HIO$_3$), ferrocyanic (H$_4$Fe(CN)$_6$), ferricyanic H$_3$Fe(CN)$_6$, hydrocyanic (HCN), sulphocyanic (HCNS), and hydrosulphuric (H$_2$S) acids, which are precipitated by the addition of silver nitrate to solutions containing an excess of free HNO$_3$.

The Second or *Neutral Silver Group* contains chromic (H$_2$CrO$_4$), dichromic (H$_2$Cr$_2$O$_7$), arsenic (H$_3$AsO$_4$), arsenous (H$_3$AsO$_3$), phosphoric (H$_3$PO$_4$), sulphurous (H$_2$SO$_3$) and oxalic (H$_2$C$_2$O$_4$) acids which are precipitated by silver nitrate from neutral solutions or solutions containing a very slight amount of acid. (Sulphurous acid is likewise contained in group three due to the appreciable solubility of silver sulphite and the oxidation by HNO$_3$ in many cases preceding the final test.)

The Third Group embraces the remainder of the common acids which can not be classified in the two preceding groups. It consists of sulphuric (H$_2$SO$_4$), sulphurous (H$_2$SO$_3$), tartaric (H$_2$C$_4$H$_4$O$_6$), chloric (HClO$_3$), bromic (HBrO$_3$), acetic (HC$_2$H$_3$O$_2$), silicic (H$_2$SiO$_3$),

hydrofluoric (HF), boric (H_3BO_3), tetraboric ($H_2B_4O_7$), nitric (HNO_3), nitrous (HNO_2), permanganic ($HMnO_4$), manganic (H_2MnO_4) and hydrosulphuric (H_2S) acids. H_2S is included in the third group on account of the difficulty with which some sulphides are decomposed by Na_2CO_3.

Before satisfactory analytical work can be done by the student a thorough knowledge of the chemical deportment of the various bases and acids and a certain amount of skill in qualitative manipulation must be obtained. For this purpose the elements of each group are studied for their most characteristic chemical similarities and differences in behavior toward reagents. The student is urged to keep constantly in mind the ultimate use of the various reactions—separation and identification of the elements.

CHAPTER IV

LABORATORY DIRECTIONS AND REVIEW EXERCISE

Note for the Student

You are responsible for the condition of your desk, your reagent bottles and apparatus. They are to be kept clean and in order. Stoppers of reagent bottles should never be placed on a shelf, table or any other place except in the necks of the bottles to which they belong, otherwise they may gather contamination and obscure or ruin future work. Should you accidentally find your desk dusty or in any way uncleanly upon coming into the laboratory clean it before starting any work and leave the desk scrupulously clean at the close of your laboratory period.

In all the groups the reactions should be studied in a comparative way. Associate the deportment of the members of each group toward each reagent, noting the changes in color, physical properties, composition, solubility, etc., of the compounds formed by each reagent. When possible you should treat all the members of each group simultaneously with each reagent, then compare results in each instance. For example in the first group the elements silver, mercurous mercury and lead occur. Take solutions of the nitrates, each in a separate test tube and add a few drops of HCl to each. Make the notations mentioned above, comparing the results obtained with silver, mercury and lead, and write the equa-

tions, underscoring the precipitates, designating the colors and physical conditions above the formula for the compounds, thus:

white, curdy

$$AgNO_3 + HCl = \underline{AgCl} + HNO_3$$

white, somewhat curdy

$$HgNO_3 + HCl = \underline{HgCl} + NHO_3$$

white

$$Pb(NO_3)_2 + 2HCl = \underline{PbCl_2} + 2HNO_3$$

colorless

$$AgCl + 2NH_4OH = AgCl \cdot 2NH_3 + 2H_2O$$

black

$$2HgCl + 2NH_4OH = \underline{HgNH_2Cl + Hg} + NH_4Cl + 2H_2O$$
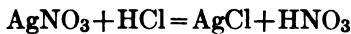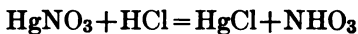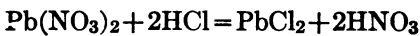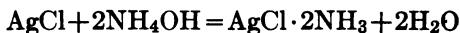
etc., etc.

If a gas is evolved, place a wave line $\sim\!\sim\!\sim$ above the compound, thus: $\widetilde{CO_2}$.

Unless stated otherwise a precipitate should always be washed thoroughly to free it from all possible contamination. When a particular wash solution is not mentioned, distilled water is always understood.

When you have completed the study of the comparison reactions and have answered the questions following each group, turn to the outlined separation scheme of the group to perform the separation of the elements. Note that the reactions used for each separation are the same as those studied previously. If any reaction is not clearly understood, review your notes, attempting to clear the obscurity by your own reasoning. If the reaction is still obscure consult with the instructor in regard to the

same. Be scientific—master each difficulty as you encounter it.

Unless some other directions are given, mix together solutions containing the elements of the group to be separated, using about three or four cubic centimeters of each of the laboratory reagents, then proceed with the analysis as directed in the outline chapters XV and XVI. For the acids use the alkali salts of each. When the presence of each member of the group has been confirmed, write in your note book a tabular form according to the following type:

AgNO₃			white AgCl		white AgCl		colorless and white AgCl.2NH₃ Add HNO₃ → AgCl
						Add NH₄OH	black HgNH₂Cl + Hg
HgNO₃	Add HCl	white HgCl	Treat with hot water	white HgCl			
					PbCl₂		Add K₂CrO₄ → PbCrO₄, yellow. Add NaOH → Pb(ONa)₂ colored yellow by chromate. Add KI → PbI₂ soluble in hot water crystallizing out in shining yellow plates on cooling.
Pb(NO₃)₂		white PbCl₂					

Lecture Notes should be used constantly *outside* the *laboratory* and all theoretical considerations regarding various reactions kept continually in mind. Lecture Note Books are not to be used while performing your laboratory work.

Keep your *Laboratory Note Book* neat and intelligible, so that the instructor can consult it at any time and excuses need not be forthcoming regarding the condition of the same. Write your notes in the laboratory at the time the experiments are performed. They are a record of what you have done and observed and are much more valuable when made at the actual time of the experiment.

Strength of Reagents

Remember that when no strength of reagent is given it is understood that you employ the dilute reagent supplied for general laboratory use. When special solutions are to be used they are always designated as such in the directions and the strength given. *Always use dilute reagents unless otherwise directed.*

EXERCISE.

1. Make a list of all the elements of each group, giving the common valences of each element.

2. How many sulphides are soluble in water; how many insoluble?

3. Name the alkalies; the alkaline earths.

4. Name and give the molecular formulas for all the common acids you can remember.

5. Write out the formulas for the sodium compounds of the common acids, and likewise the chlorides of the bases in the common valences.

6. Why should a large excess of reagent always be avoided?

7. What do you understand by the following terms: " soluble " and " insoluble," " residue," " occlusion," " osmosis," " gas," " liquid," " solid," " chemical affinity," " amalgam," " alloy," " allotropy," " electrolysis," " electro-chemical series," " emulsion" " indicator," " insulator."

8. (*a*) Write the equation representing the reaction between $HgNO_3$ and $NaCl$ and explain the reaction in terms of the ionization of the compounds. (*b*) Do likewise with $H_2S + BiCl_3$.

9. What is the " Law of Definite Proportions;" the " Law of Multiple Proportions;" " Henry's Law;" " Law

of Hess;" " Law of Lavoisier and Laplace;" " Berthelot's Law of Maximum Work?"

10. Pass H_2S through a solution of HNO_3. What happens? Write the equation involved. If you used some soluble nitrate would the reaction be similar? What two products always result if either nitric acid or a nitrate is used?

11. Name the metals and the non-metals. Why are they so classed?

12. Write equations illustrating what happens when
  (1) water reacts with a metal.
  (2) water reacts with a non-metal.
  (3) water reacts with the oxide of a metal.
  (4) water reacts with the oxide of a non-metal.
  (5) an acid reacts with the oxide of a non-metal.
  (6) an acid reacts with the oxide of a metal.
  (7) an acid reacts with a metal.
  (8) a strong acid reacts with a salt of a weaker acid.
  (9) A weak acid reacts with a salt of a stronger acid.
  (10) an alkali reacts with a metal.
  (11) an alkali reacts with an oxide of a non metal.
  (12) an alkali reacts with an oxide of a metal.
  (13) a strong alkali reacts with a salt of a weaker base.
  (14) a weak base reacts with a salt of a stronger base.
  (15) a gas reacts with a gas.
  (16) a gas reacts with a liquid.
  (17) a gas reacts with a solid.
  (18) a liquid reacts with a liquid.
  (19) a liquid reacts with a solid.
  (20) a solid reacts with a solid.

Which examples given for the first fourteen also apply for the last six equations asked for?

13. In what groups of Mendelejeff's Periodic Table are the following elements placed and why: silver, chlorine, sodium, barium, aluminum, tin, sulphur, phosphorus and nickel?

14. (a) Enumerate all the oxides you can remember that are insoluble in water; those soluble in this medium. (b) Do the same for the carbonates.

15. (a) What is a polariscope, a spectroscope, a blow-pipe? (b) How do you interpret " distillation," " sublimation," " volatilization," " crystallization," " decantation," " precipitation," " filtration," " immiscible solvent"?

16. Compare the chemistry of water with that of hydrogen sulphide, of sulphuric acid with chromic acid, and of ammonium hydroxide with potassium hydroxide.

(If you are unable to perform any of the above exercises, consult any general chemistry in the library. If you find the exercises difficult review a good text on general chemistry after consultation with the instructor. The following work in qualitative analysis presupposes a good foundation of general chemistry and this brief review is given at this time to point out to you any weakness in preparation.)

CHAPTER V

THE BASES

Hydrochloric Acid Group

GROUP I

REACTIONS of solutions containing salts of silver and mercurous mercury each of valence one, and of lead of valence two. Try each of the following preliminary reactions, using acetate or nitrate salt solutions.

The student is reminded that most of these reactions are ionic reactions and that the same results are obtained generally when testing for a metallic ion no matter what the source of the acid ion is, and vice versa. For example, silver chloride will be precipitated no matter what salt of silver you take in solution so long as it yields silver ions. Silver chloride will be precipitated also from any such silver salt solutions by any chloride solution which gives chloride ions, as sodium or calcium chlorides. The reagent with which a given test is directed to be carried out is the one ordinarily used, but not very often is it the only one by which the result indicated may be obtained.

HCl Precipitates:

AgCl, white, curdy; on exposure to light changes from white to lavender, then black; insoluble in water; soluble in NH_4OH forming $AgCl \cdot 3NH_3$ or $2AgCl \cdot 3NH_3$.[1] Nitric

[1] $AgCl \cdot 3NH_3$ exists at a temperature below 15°, while above 20° $2AgCl \cdot 3NH_3$ is the stable form.

acid removes the NH_3 from this solution, reprecipitating AgCl.

HgCl, white; not changed appreciably on exposure to light; insoluble in water; changed by ammonia to a black mixture of Hg and $HgNH_2Cl$, mercuric chloramide.

$PbCl_2$, white, flocculent, from not too dilute solutions; readily soluble in hot water from which it crystallizes in long needles when the solution is cooled; somewhat soluble in cold water. $PbCl_2$ is not soluble in ammonia.

K_2CrO_4 Precipitates:

Ag_2CrO_4, red, decomposed by NaOH.

Hg_2CrO_4, on boiling orange yellow; decomposed by NaOH.

$PbCrO_4$, yellow; easily soluble in considerable excess of NaOH, forming $Pb(ONa)_2$.

KI Precipitates:

AgI, yellow; soluble in excess of concentrated reagent forming $KI \cdot AgI$, decomposed by dilution.

HgI, yellowish green; decomposed by alkali iodides forming Hg and HgI_2, the latter dissolving in excess of alkali iodide to form $HgI_2 \cdot 2KI$.

PbI_2, yellow; soluble in hot water, crystallizing out in characteristic shining plates on cooling.

H_2S Precipitates:

Ag_2S, black; changed by hot dilute HNO_3 to sulphur and $AgNO_3$, which is soluble.

Hg and HgS, black; insoluble in HNO_3.

PbS, black; soluble in dilute HNO_3; oxidized by hot fuming HNO_3 to $PbSO_4$, white.

KOH or NaOH Precipitates:

Ag_2O, grayish brown; soluble in acids; soluble in alkali cyanide solutions forming soluble salts such as

$KCN \cdot AgCN$; soluble in a solution of $Na_2S_2O_3$, forming $Ag_2S_2O_3 \cdot 2Na_2S_2O_3$.

Hg_2O, black; insoluble in the alkalies; transposed by acids to the corresponding salts.

$Pb_2O(OH)_2$, white, soluble in excess of reagent, forming $Pb(OK)_2$ or $Pb(ONa)_2$.

NH_4OH Precipitates:

$AgOH$, white, changing to Ag_2O, grayish brown; soluble in excess of reagent; not precipitated in presence of ammonium salts.

$Hg + Hg_2N \cdot NO_3$, a black mixture, from nitrate solutions.

White basic salts of lead, soluble in large excess of concentrated reagent.

Na_2CO_3 Precipitates:

Ag_2CO_3, white with a yellow tinge: slightly soluble in water and excess of reagent; soluble in NH_4OH and $(NH_4)_2CO_3$.

Hg_2CO_3, gray, unstable, changing to a mixture of Hg, HgO, and CO_2.

$Pb_3(OH)_2(CO_3)_2$, white basic carbonate; soluble in large excess of concentrated reagent.

$(NH_4)_2$ S Precipitates:

Ag_2S, black.

$HgS + Hg$, black.

PbS, black.

H_2SO_4 Precipitates:

Ag_2SO_4, from concentrated solutions; white, crystalline; somewhat soluble in excess of reagent.

Hg_2SO_4, white; by boiling with an excess of sulphuric acid soluble mercuric sulphate is formed; boiling with water produces an insoluble basic sulphate.

$PbSO_4$, white, crystalline; almost insoluble in water; partially soluble in HNO_3; readily soluble in ammonium acetate containing a little free acetic acid.

SnCl₂ Precipitates:

AgCl, white; alkali stannites reduce silver salts in solution to metallic silver, dark.

HgCl, white at first, then with an excess of reagent Hg, black.

No reaction with lead salts.

Replacement by Metals:

Lead precipitates Ag, dark, and Hg, black, from their solutions.

Mercury precipitates Ag, dark.

Zinc precipitates Ag, dark, Hg, black, and Pb, dark, from their solutions.

EXERCISE.

1. Given silver and mercury in a solution. How can you separate and identify each? Likewise silver and lead; mercury and lead.

2. Is hydrogen sulphide gas ever liberated as such when a sulphide is treated with nitric acid? Explain.

3. Could metallic mercury be used as a test for silver in the presence of lead and mercury in the form of nitrates? How?

4. Under what conditions could stannous chloride be used in testing for mercury?

5. Does any reaction take place when lead chloride dissolves in water?

6. Can the reagent KI be used to detect any one of the elements of this group in the presence of the other two? How?

7. Discuss the precipitation of AgCl, $PbCrO_4$, HgI and Ag_2S in light of ionization and the mass law.

CHAPTER VI

THE BASES

Hydrogen Sulphide Group

GROUP II

REACTIONS of solutions containing salts of mercuric mercury, lead, copper and cadmium, each of valence two, of bismuth of valence three, of arsenic and antimony of valences three and five and of tin of valences two and four. Try these tests, using chlorides or nitrates in solution in each case except arsenic. For arsenic use the sodium salts of H_3AsO_3 and H_3AsO_4. These are mostly ionic reactions again and the remarks at the head of Chapter V apply here.

H_2S Precipitates (from slightly acid solutions):

HgS, black; insoluble in hot conc. HNO_3; changed by prolonged action of conc. HNO_3 to $Hg(NO_3)_2 \cdot 2HgS$, white, insoluble in HNO_3. Aqua regia turns both compounds into soluble $HgCl_2$ and free sulphur. HgS is insoluble in $(NH_4)_2 S_x$.

PbS, black, insoluble in $(NH_4)_2S_x$; soluble in dilute HNO_3; oxidized by hot fuming HNO_3 to $PbSO_4$, white.

CuS, black, soluble in hot HNO_3; insoluble in hot dilute H_2SO_4; only slightly soluble in $(NH_4)_2S_x$, from which solution dilute acids precipitate a yellowish brown compound, the composition of which is not definitely known.

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CuS is soluble in KCN, forming $CuCN \cdot KCN$, liberating $(CN)_2$ gas (Poison).

CdS, light yellow to orange; easily soluble in HCl or hot dilute H_2SO_4; changed by hot HNO_3 to soluble $Cd(NO_3)_2$ and free sulphur. CdS is insoluble in $(NH_4)_2S_x$ and KCN.

Bi_2S_3, dark brown; changed to soluble $Bi(NO_3)_3$ with hot HNO_3; insoluble in $(NH_4)_2S_x$.

As_2S_3, lemon yellow; almost insoluble in warm concentrated HCl; oxidized by a crystal of $KClO_3$ and hot HCl, or by hot HNO_3, to H_3AsO_4, which is soluble. As_2S_3 is soluble in $(NH_4)_2S_x$, forming salts such as $(NH_4)_3AsS_4$, from which HCl precipitates As_2S_5. Hot and cold $(NH_4)_2CO_3$, hot 5% Na_2CO_3, and 10% NaOH dissolve As_2S_3, forming such salts as $NH_4AsO_2 + NH_4AsS_2$ or $(NH_4)_3AsO_3 + (NH_4)_3AsS_3$, or the corresponding sodium salts, from which solutions dilute acids reprecipitate As_2S_3.

As_2S_5, lemon yellow; slowly precipitated when H_2S is rapidly passed through a solution of arsenic acid. If passed slowly H_2S reduces the arsenic to arsenous acid and then precipitates As_2S_3. As_2S_5 is soluble in $(NH_4)_2S_x$, forming salts as $(NH_4)_3AsS_4$, reprecipitating upon addition of dilute acids. As_2S_5 dissolves in hot and cold $(NH_4)_2CO_3$, hot 5% Na_2CO_3, and 10% NaOH, forming salts as $(NH_4)_3AsO_4 + (NH_4)_3AsS_4$ or $(NH_4)_3AsS_4 + (NH_4)_3AsO_3S$, or the sodium salts, dilute acids reprecipitating the sulphide.

Sb_2S_3, orange red, from moderately acid solutions of Sb^{III} and Sb^{V}; soluble in warm conc. HCl; oxidized by $KClO_3$ and hot conc. HCl, forming sulphur and $SbCl_5$; soluble in $(NH_4)_2S_x$, forming salts such as $(NH_4)_3SbS_4$, from which dilute acids precipitate Sb_2S_3 and sulphur. Sb_2S_3 dissolves in hot 5% Na_2CO_3 and 10% NaOH, form-

ing compounds similar to those of arsenous arsenic, re-precipitated by dilute acids. It is practically insoluble in $(NH_4)_2CO_3$.

SnS, dark brown; soluble in warm conc. HCl; oxidized by $KClO_3$ and hot conc. HCl to sulphur and soluble $SnCl_4$; soluble in $(NH_4)_2S_x$, forming such salts as $(NH_4)_2SnS_3$, from which dilute acids precipitate SnS_2, yellow. SnS is not affected by $(NH_4)_2CO_3$ nor 5% Na_2CO_3 but dissolves in 10% NaOH, forming $Na_2SnO_2 +$ Na_2SnS_2, reprecipitated by dilute acids.

SnS_2, yellow; precipitated from solutions containing a moderate amount of HCl; soluble in $(NH_4)_2S$ or $(NH_4)_2S_x$, forming salts as $(NH_4)_2SnS_3$, dilute acids re-precipitating the sulphide. SnS_2 dissolves in 5% Na_2CO_3 and 10% NaOH, forming salts as $Na_2SnO_3 + Na_2SnS_3$, reprecipitated by addition of a dilute acid. SnS_2 is like-wise soluble in warm conc. HCl.

NOTES

1. If H_2S passes slowly through a solution of mercuric chloride, first $HgCl_2 \cdot 2HgS$, white, is precipitated; this changes to yellow and brown compounds and finally to HgS, black, as the HgS increases in proportion to $HgCl_2$ in double combination. Some of the intermediate com-pounds are soluble in HNO_3, but are converted to HgS by $(NH_4)_2S_x$. Mercuric chloride has a distinct volatility, so much so in fact that mercuric chloride solutions can not be evaporated without loss of mercury.

2. If the lead solution contains a large amount of HCl, $PbCl_2 \cdot 2PbS$, brick red may be precipitated.

3. Moist CuS will oxidize to $CuSO_4$ when exposed to air.

4. When KCN is added in small quantity to a solution containing cadmium and copper $Cd(CN)_2$ and $Cu(CN)_2$

form at first, the latter decomposing into CuCN and $(CN)_2$, an excess of reagent converting these to soluble K_2CdCN_4 and $KCu(CN)_2$. $KCu(CN)_2$ is not decomposed by H_2S, while $K_2Cd(CN)_4$ is, hence Cd precipitates as sulphide.

5. The completeness of the precipitation of these sulphides depends on the concentration of acid in the solution   If the solution is too strongly acid cadmium, stannous tin or lead may be incompletely precipitated. If the solution is neutral or alkaline arsenic, antimony or tin may not be precipitated, due to the formation of the soluble thio-salts of these elements.   In the group separation the degree of acidity is regulated to give complete precipitation of the members of this group,—one part of dilute HCl to ten of water.   Treatment with H_2S gives a reversible reaction.

$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 + 6HCl$$
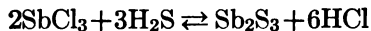
In dilute acid solutions the action proceeds toward the right, but in strong acid solutions the action reverts to the left, the sulphides tending to dissolve as rapidly as formed.   In alkaline solutions alkali sulphides are produced keeping certain members of the group in solution, thus: $2NaOH + H_2S = Na_2S + 2H_2O$. $3Na_2S + As_2S_5 = 2Na_3AsS_4$.   Precipitation may not take place in neutral or alkaline solutions because of a reaction similar to the following· $3H_2S + Na_3AsO_3 = Na_3AsS_3 + 3H_2O$.

6. $(NH_4)_2S_x$, ammonium polysulphide is a yellow solution of varying composition, the x representing an indefinite number of sulphur atoms in the molecule, usually from 2 to 5.   The reagent is unstable, decomposing into S and colorless ammonium sulphide, $(NH_4)_2S$.   The latter reagent can not be used to advantage, as SnS is insoluble and Sb_2S_3 soluble with difficulty in this reagent.

NH$_4$OH Precipitates (from their chloride solutions):
HgNH$_2$Cl, white; if the nitrate is used Hg$_2$N·NO$_3$ is precipitated, also white.

CuCl$_2$·Cu(OH)$_2$, light blue basic salt; soluble in excess forming CuCl$_2$4NH$_3$, deep blue, bleached by KCN. (Caution.)

Cd(OH)$_2$, white; soluble in excess forming Cd(Cl)$_2$·4NH$_3$, colorless.

Bi(OH)$_3$, or a basic salt, white; insoluble in excess; soluble in dilute acids.

PbCl$_2$·Pb(OH)$_2$, white; insoluble in excess; also insoluble in water.

Sb(OH)$_3$, white; insoluble in excess; soluble in acids.

SbO(OH)$_3$, white; insoluble in excess; soluble in acids.

Sn(OH)$_2$, insoluble in excess; soluble in KOH or NaOH, forming stannites as Sn(OK$_2$).

Sn(OH)$_4$, stannic acid, white, gelatinous; soluble in KOH or NaOH, forming stannates as Sn(OK)$_4$.

Arsenic compounds are not precipitated by NH$_4$OH.

NOTE.—KCN, when added to CuSO$_4$·4NH$_3$ solution or other ammoniacal copper salt solutions, decolorizes the same, forming compounds similar to those mentioned on page 44 in the test for cadmium.

Reduction by SnCl$_2$:

SnCl$_2$ reduces HgCl$_2$ to HgCl, a white precipitate. If an excess of SnCl$_2$ is added the HgCl is more or less reduced to metallic mercury.

A concentrated solution of SnCl$_2$ and conc. HCl in equal parts boiled with a few drops of H$_3$AsO$_3$ reduces the latter to elementary arsenic (the solution darkens). Metallic tin present facilitates the reaction.

In case tin foil is used antimony from antimonous solutions is deposited as an even velvety black coating on the tin; arsenic deposits unevenly under like conditions.

Metallic Iron Reduces:

Mercuric salts to metal, dark gray.   Mercuric chloride forms HgCl first, then the metal.

Copper salts to metal.   If a strip of bright iron is immersed in a copper chloride solution acidulated with HCl a bright copper coating is recognizable even in dilutions of 1 : 120,000.

Bismuth salts to metal, forming a spongy precipitate.

Lead salts to metallic lead from acetate or chloride solutions.

Cadmium salts give no action with metallic iron.

Antimony from chloride solutions to the metallic state upon the addition of HCl and warming.

Stannic chloride to stannous chloride.

Arsenic^V is reduced to arsenic^{III} under these conditions.

H_2O Added in Large Quantities Precipitates:

$BiOCl$, $(BiO)_2SO_4$, $BiONO_3$, etc., white, from solutions that do not contain too much free acid.   These salts are soluble in inorganic acids.

$SbOCl$, etc., white, from solutions containing little free acid.   Soluble in inorganic acids.

NOTE.—Sometimes a reaction occurs, forming the hydrated oxides of tin from a cause similar to the above. Boiling neutral solutions of the tin salts will produce this effect.   The addition of salts such as NH_4NO_3 also facilitates hydrolysis.

KI Precipitates:

HgI_2, red; soluble in excess forming $HgI_2 \cdot 2KI$, colorless.

CuI, white, colored brown by the liberated iodine.

PbI_2, yellow; soluble in hot water, crystallizing on cooling in shining plates.

BiI_3, brownish black; soluble in excess of reagent.

SbI_3, yellow, from solutions not too strongly acid; soluble in HCl.

A yellow compound in concentrated solutions of stannous chloride, turning orange on addition of more reagent; soluble in large excess of reagent, sparingly soluble in water.

SnI_4, yellow, from very concentrated solutions; soluble in water.

KI gives no reaction with dilute arsenous solutions. When added to arsenic solutions and antimonic solutions reduction to the arsenous and antimonous state occurs with the liberation of iodine.

KCN Precipitates:

$Hg(CN)_2$, white; soluble in water; soluble in excess forming $Hg(CN)_2 \cdot 2KCN$.

$Pb(CN)_2$, white, slightly soluble in excess of reagent.

$Cu(CN)_2$, yellowish green; soluble in excess forming colorless $CuCN \cdot KCN$. KCN solution bleaches the blue color of copper ammonio-salts due to a similar reaction.

$Bi(OH)_3$, white. The cyanide is first formed but hydrolyzes, forming the hydroxide.

$Cd(CN)_2$, white, changing to soluble $K_2Cd(CN)_4$ with excess of reagent.

No characteristic reactions occur with arsenic, antimony and tin solutions.

KOH or NaOH Precipitates:

A reddish brown basic salt when added in small amounts to mercuric salts and HgO, orange-yellow with excess of reagent.

$Pb(OH)_2$, white; soluble in excess, forming such salts as $Pb(OK)_2$ or $Pb(ONa)_2$.

$Bi(OH)_3$, white; insoluble in excess of reagent.

$Cu(OH)_2$, deep blue, changed to black CuO on boiling.

$Sb(OH)_3$, white, soluble in excess, forming $Sb(OK)_3$ or $Sb(ONa)_3$.

$SbO(OH)_3$, white, soluble in excess, forming $SbO(OK)_3$ or $SbO(ONa)_3$

$Sn(OH)_2$, white, soluble in excess, forming $Sn(OK)_2$ or $Sn(ONa)_2$.

$Sn(OH)_4$, white, soluble in excess, forming $Sn(OK)_4$ or $Sn(ONa)_4$.

The fixed alkalies give no precipitates with arsenous or arsenic solutions, the corresponding hydroxides and the alkali arsenites and arsenates being soluble.

Na_2CO_3 Precipitates:

A reddish brown basic carbonate of mercury.

$Pb_3(OH)_2(CO_3)_2$, white, insoluble in excess of reagent.

$Cu_2(OH)_2CO_3$, greenish blue; readily soluble in acids; boiling the solution forms black CuO.

$CdCO_3$, white; insoluble in excess of reagent; readily soluble in dilute acids.

$(BiO)_2CO_3$, white; insoluble in excess of reagent; readily soluble in dilute acids.

$Sb(OH)_3$, white; soluble in large excess of reagent.

$SbO(OH)_3$, white; soluble in large excess of reagent.

$Sn (OH)_2$, white; soluble in large excess of reagent.

$Sn(OH)_4$, white; soluble in large excess of reagent.

No precipitate forms with arsenic or arsenous solutions.

$K_4Fe(CN)_6$ Precipitates:

A white precipitate from mercury solutions; decomposed on boiling.

$Pb_2Fe(CN)_6$, white; soluble in water and dilute acids.

$Bi_4[Fe(CN)_6]_3$, yellowish white; soluble in dilute acids.

$Cu_2Fe(CN)_6$, reddish brown; characteristic; insoluble in acids; decomposed by the alkalies.

$Cd_2Fe(CN)_6$, white, insoluble in dilute acids, decomposed by alkalies.

No characteristic reactions occur with arsenic.

$Sn_2Fe(CN)_6$, white; insoluble in water; soluble in concentrated HCl.

Stannic tin as a greenish white precipitate; soluble in hot HCl; reprecipitated on cooling.

With antimonous chloride a white precipitate, soluble in HCl or alkali hydroxides.

Na_2CO_3 Fusion on Charcoal Produces:

Globules of metallic mercury.

Globules of metallic lead with oxides, yellow to red, as coating on the outer edges.

Metallic copper, malleable; or Cu_2O, red, brittle.

Metallic cadmium, gray, easily oxidized, forming CdO, brown, as a coating on the charcoal.

Metallic bismuth, gray, brittle, with a yellowish oxide, Bi_2O_3, around the edges.

Arsenous or arsenic oxides volatilize as As_2O_3 readily when heated and give a white sublimate distant from the spot of fusion.

Antimonous and antimonic oxides volatilize as Sb_2O_3 when heated and give a white sublimate near the spot of fusion.

Malleable lustrous globules of metallic tin. Some white SnO_2 collects as incrustation near the fusion.

Zn+HCl Precipitates:

HgCl, white, then metallic mercury, black.

Metallic lead, black, if precipitated rapidly, but steel gray if precipitated more slowly.

Metallic bismuth, black.

Metallic copper, red or yellow, depending on the amount.

Metallic cadmium, gray.

Zn+HCl With

(Granulated zinc is placed in a test tube containing an HCl solution of the substance to be tested. A cotton plug moistened with lead acetate solution is inserted in the tube to absorb any hydrogen sulphide formed as impurity. A crystal of silver nitrate is placed on a filter paper fitted over the mouth of the tube and action noted.)

Arsenous and arsenic solutions cause the crystal to turn yellow, due to the action of the volatile arsine, AsH_3, on the $AgNO_3$, forming $3AgNO_3 \cdot AsAg_3$, then black due to the formation of metallic silver.

Antimony solutions evolve stibine, SbH_3, which forms black Ag_3Sb (called antimonous argentide or silver antimonide) with the $AgNO_3$ immediately.

Stannic and stannous salts deposit metallic tin on the zinc.

NaOH or KOH+Al Reaction

Furnishing hydrogen instead of Zn+HCl in above tests give the same results with arsenous solutions, but arsenic solutions are not effected. No SbH_3 forms in the alkaline reaction but antimony is deposited, mostly on the aluminum. Tin may be deposited from stannous or stannic solutions, but not necessarily.

$(NH_4)_2MoO_4$ Precipitates:

From a nitric acid solution of arsenic when warmed to not over 70°, $(NH_4)_3AsO_4 \cdot 12MoO_3$, lemon yellow, characteristic. (Phosphoric acid also gives a similar precipitate under the same conditions.)

K_2SnO_2 or Na_2SnO_2

Hot, when added to bismuth solutions or moist $Bi(OH)_3$ precipitates black metallic bismuth. The stannite is made by adding an excess of NaOH or KOH to a solution of

$SnCl_2$ until the precipitate which first forms just redissolves again.

$K_2Cr_2O_7$ or K_2CrO_4 Precipitates:

$CdCrO_4$, yellow, from very concentrated solutions only; soluble in water.

$PbCrO_4$, yellow; easily soluble in excess of $NaOH$. forming $Pb(ONa)_2$.

$3BiO_3 \cdot 2CrO_3$, yellow; insoluble in excess of $NaOH$; soluble in dilute acids.

A yellow compound with $Hg(NO_3)_2$.

Copper does not give a precipitate with $K_2Cr_2O_7$ or K_2CrO_4.

Potassium dichromate oxidizes arsenous, antimonous and stannous salts to their higher state of oxidation, in acid solutions, but forms no precipitates. Other oxidizing agents, such as $KMnO_4$, Cl_2, etc., perform the same function.

EXERCISE

1. Due to what property of arsenic, antimony and tin can these elements be separated from the remainder of the elements of this group?

2. Name two methods of separating copper from cadmium.

3. Name two methods of separating lead from copper.

4. Give two schemes of detecting arsenic and tin in the presence of each other.

5. Give two schemes of detecting arsenic and antimony in the presence of each other.

6. Write out briefly a scheme of separating As, Sb, and Sn by use of alkaline solutions.

7. Given a solution of $BiCl_3$ and $CuCl_2$, what is a simple test for the former and for the latter?

8. Given a solution of H_3AsO_4 and $CdCl_2$, what is a simple test for the former and for the latter?

9. What reactions can be utilized in detecting stannous in presence of stannic tin?

10. Given a solution of $AgNO_3$ and $Bi(NO_3)_3$, give a simple test for the former.

11. Given a solution containing lead, bismuth, cadmium and copper, how can you separate and identify each?

12. How can mercurous and mercuric mercury in solution be distinguished?

13. Discuss the precipitation of Sb_2S_3 from the viewpoint of ionization and the mass effect of the reagents used.

14. Explain in the language of ionization the precipitation of cadmium sulphide and not copper sulphide from cyanide solutions with hydrogen sulphide.

CHAPTER VII

THE BASES

Ammonium Sulphide Group

GROUP III

REACTIONS of solutions containing nickel, cobalt, ferrous iron, manganese and zinc having the valence of two, ferric iron, aluminum and chromium with the valence of three, and tetravalent titanium. Use the chloride, sulphate, or nitrate salt solutions for the preliminary reactions.

$(NH_4)_2S$ Precipitates from Slightly Ammoniacal Solutions:

NiS, black; exceedingly slowly soluble in cold normal HCl[1]; changed by aqua regia to free sulphur and soluble NiCl$_2$.

CoS, black; insoluble in excess; exceedingly slowly soluble in cold normal HCl; attacked by aqua regia, forming sulphur and CoCl$_2$, soluble.

FeS, black; from ferrous and ferric solutions of iron; attacked by hot HNO$_3$, forming sulphur and soluble Fe(NO$_3$)$_3$. FeS is slowly soluble in cold normal HCl.

Cr(OH)$_3$, green; from all salts of chromium of all valences, sulphur being liberated when reaction takes

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[1] Dilute one volume of the dilute HCl with three volumes of water.

place with chromates; precipitation from the higher oxidation stages of chromium takes place slowly; soluble in cold normal HCl.

MnS, pink; from manganous salts, manganates and permanganates, precipitation proceeding slowly in the case of the last two; soluble in dilute inorganic or acetic acids.

$Al(OH)_3$, white; soluble with difficulty in NH_4OH, probably forming $Al(ONH_4)_3$, reprecipitating on warming; soluble in dilute inorganic acids.

ZnS, white; when freshly precipitated is soluble in dilute inorganic acids; only very slightly soluble in acetic acid.

$Ti(OH)_4$, white, from cold solutions; insoluble in excess of reagent. From hot solutions $TiO(OH)_2$, white, precipitates. This hydrate is soluble with difficulty in acids, especially in dilute. Concentrated HCl or H_2SO_4 dissolves it slowly. Practically insoluble in HNO_3 and $HC_2H_3O_2$.

NOTES

1. The sulphides of this group are distinguished from those of the preceding group in that they are precipitated from a neutral or alkaline solution by hydrogen sulphide or an alkaline sulphide instead of by hydrogen sulphide in an acid solution. The elements of preceding groups, mercury, silver, lead, cadmium, bismuth and copper will likewise precipitate under these conditions, but most of the arsenic, antimony and tin will remain in solution. If a small amount of ammonium polysulphide is present the last three will be held completely in solution. The polysulphide should not be used, as it exerts a solvent action on NiS giving a brown solution and also tends to precipitate large quantities of sulphur.

2. NiS is somewhat soluble in excess of $(NH_4)_2S$ more readily in the presence of NH_4OH, forming a dark brown solution from which NiS is precipitated if the solution is boiled and solvent removed. Moist NiS is oxidized by the air to $NiSO_4$, soluble.

3. Moist CoS is oxidized by the air to $CoSO_4$, soluble.

4. FeS on exposure to the moist air forms soluble $FeSO_4$ and insoluble basic ferric sulphate, $Fe_2(OH)_2(SO_4)_2$, or $Fe_2O(SO_4)_2$, brown.

5. $Cr(OH)_3$ is soluble with difficulty in NH_4OH in the presence of NH_4Cl, from which $Cr(OH)_3$ is reprecipitated on boiling.

6. MnS oxidizes to a brown color in air, forming Mn_2O_3, $MnSO_4$ and S. Oxalates and tartrates tend to prevent precipitation. (See note 2, page 58.)

7. H_2S precipitates ZnS incompletely from neutral solutions or solutions only very slightly acid with mineral acids.

KOH or NaOH Precipitates:

$Ni(OH)_2$, apple green; insoluble in excess of reagent. $Ni(OH)_2$ is oxidized by boiling with an excess of NaOH and bromine water to $Ni(OH)_3$, black. If this precipitate is filtered and boiled with NH_4OH, it is reduced to $Ni(OH)_2$, nitrogen being liberated. If NH_4Cl is present $Ni(OH)_2$ dissolves, forming $NiCl_2 \cdot 4NH_3$, blue.

When $Ni(OH)_3$, after washing with hot water until the filtrate gives no precipitate with $AgNO_3$, is treated with a hot solution of KI containing no free iodine (made by dissolving some crystals of KI in water and used immediately) the nickelic is reduced to the nickelous state and free iodine will be found in the filtrate upon shaking with a few drops of CS_2 in a test tube.

$Co(OH)Cl$, blue basic salt; when warmed with alkali it changes to $Co(OH)_2$, pink. $Co(OH)_2$ may be oxidized with NaOH and bromine water by boiling to $Co(OH)_3$, black. $Co(OH)_3$ is not reduced by boiling with NH_4OH. $Co(OH)_3$ is not reduced by hot KI, as is $Ni(OH)_3$.

$Fe(OH)_2$, white, from ferrous salt solutions; immediately oxidizes to a dirty green compound on exposure to air, and finally becomes $Fe(OH)_3$, reddish brown; changed by $(NH_4)_2S$ to FeS.

$Fe(OH)_3$, reddish brown, gelatinous, from ferric salt solutions; transformed by $(NH_4)_2S$ into FeS.

$Mn(OH)_3$, from manganese salt solutions, white; oxidizes to $MnO(OH)_2$, which reacts with $Mn(OH)_2$, forming Mn_2O_3; these compounds are dark brown.

$Zn(OH)_2$, white, gelatinous; soluble in excess of reagent, forming $Zn(OK)_2$ or $Zn(ONa)_2$.

$Cr(OH)_3$, grayish green, gelatinous; easily soluble in excess of reagent, forming $Cr(OK)_3$ or $Cr(ONa)_3$, giving a green color to the solution. When this solution is boiled $Cr(OH)_3$ is reprecipitated. (If the solution is dilute or an ammonium salt is present the reprecipitation takes place more readily.) $Cr(OH)_3$ is soluble in dilute inorganic acids.

$Al(OH)_3$, white, gelatinous; easily soluble in excess of reagent, forming $Al(OK)_3$ or $Al(ONa)_3$. On the addition of NH_4Cl and boiling, $Al(OH)_3$ is reprecipitated. $Al(OH)_3$ when freshly precipitated is easily soluble, in dilute inorganic acids.

$Ti(OH)_4$ or $TiO(OH)_2$, white, depending on the temperature of precipitation; practically insoluble in excess of reagent, soluble in mineral acids. (See $(NH_4)_2S$ reaction.)

Na_2O_2 Converts:

(The solution is made alkaline with NaOH and the Na_2O_2 added to the solution or suspension produced.)

$Ni(OH)_2$ partially to $Ni(OH)_3$, black.

$Co(OH)_2$ to $Co(OH)_3$, black.

$Fe(OH)_2$ to $Fe(OH)_3$, red brown.

$Mn(OH)_2$ to MnO_2, hydrated, brown.

Soluble $Cr(ONa)_3$, green, to soluble Na_2CrO_4, yellow.

Na_2O_2 has no effect on sodium zincate or sodium aluminate.

$Ti(OH)_4$ or $TiO(OH)_2$, white, partially to a yellow soluble sodium salt, probably pertitanate (Na_2TiO_4?), which, however, is decomposed on boiling, causing a complete precipitation of the titanium, as $TiO(OH)_2$. Na_2O_2 is also decomposed on boiling, forming NaOH and O_2. (See note 3, page 58.)

NH_4OH Precipitates:

$Ni(OH)_2$ or $Ni_2(OH)_2SO_4$, green; soluble in NH_4OH in the presence of ammonium salts, forming such salts as $NiSO_4 \cdot 4NH_3$, changed to NiS by $(NH_4)_2S$.

$Co_2(OH)_2SO_4$, blue basic salt; easily soluble in NH_4OH, forming such salts as $CoSO_4 \cdot 4NH_3$. This solution quickly assumes a red color, through oxidation by the air to complex cobaltic compounds. These solutions and precipitates are changed by $(NH_4)_2S$ to CoS.

$Fe(OH)_2$, white, from ferrous salt solutions; incompletely precipitated in neutral solutions, part of the iron remaining in solution as a double salt, such as $FeSO_4 \cdot (NH_4)_2SO_4$ or $FeCl_2 \cdot 2NH_4Cl$. If sufficient ammonium salts are present no ferrous hydroxide will be precipitated. $(NH_4)_2S$ forms FeS from these solutions and precipitates.

$Fe(OH)_3$, red brown, gelatinous, from ferric salt solutions.

$Mn(OH)_2$, white, from neutral solutions in the absence of ammonium salts, one-half of the manganese remaining in solution, as $MnCl_2 \cdot 2NH_4Cl$ or similar salts. If sufficient ammonium salts are present no manganous hydroxide will be precipitated. $(NH_4)_2S$ changes these compounds to MnS.

$Al(OH)_3$, white, gelatinous; soluble with difficulty in NH_4OH, forming probably $Al(ONH_4)_3$, $Al(OH)_3$ reprecipitating on boiling.

$Cr(OH)_3$, grayish green, gelatinous; soluble with difficulty in excess of reagent with NH_4Cl, yielding a pinkish lavender filtrate, containing mostly $CrCl_3 \cdot 4NH_3$. $Cr(OH)_3$ is reprecipitated on boiling.

$Zn(OH)_2$, white, gelatinous, from solutions containing no ammonium salts; soluble in excess of reagent and NH_4Cl, forming $ZnCl_2 \cdot 2NH_4Cl$. These compounds are converted to ZnS by $(NH_4)_2S$.

$Ti(OH)_4$ or $TiO(OH)_2$, white, insoluble in excess of reagent. (See $(NH_4)_2S$ reaction.) If H_2O_2 is added to the suspension it turns yellow, due probably to oxidation to TiO_3, hydrated.

NOTES

1. $Fe(OH)_2$ oxidizes through the stages mentioned under NaOH treatment. As the double salt in solution oxidizes ferric hydroxide is precipitated.

2. Upon oxidation $MnO(OH)_2$, changing to Mn_2O_3, is precipitated. Mn_2O_3 is gradually changed to MnO_2, hydrated.

3. The hydroxides enumerated above are given as $Fe(OH)_3$, $Al(OH)_3$, etc., such being the conventional form of writing them. However, these formulas should

not be construed as literally correct, inasmuch as the amount of hydration varies with the procedure used in precipitation.

Na_2CO_3 Precipitates:

A basic cobaltous carbonate, peach red; boiling causes a loss of CO_2, and a color change to violet or blue, depending on the quantity of reagent in excess.

Green basic nickelous carbonates; soluble in ammonium salts or ammonium hydroxide, imparting a blue or greenish blue color to the solution.

$MnCO_3$, white, oxidized in the air to brown manganic hydroxide, which gradually forms hydrated manganese dioxide.

Zinc basic carbonate, white; soluble in the alkalies and ammonium carbonate.

$FeCO_3$, white, from ferrous solutions free from ferric; rapidly changes to ferric hydroxide.

$Fe(OH)_3$, red brown, from ferric solutions.

$Al(OH)_3$, white.

$Cr(OH)_3$, green.

$Ti(OH)_4$ or $TiO(OH)_2$, white.

H_2S Precipitates:

NiS, black, from acetic acid solutions; quite readily soluble in concentrated HCl when freshly precipitated; exceedingly slowly soluble in cold normal HCl; readily soluble in aqua regia; not precipitated from solutions containing a moderate amount of HCl.

CoS, black, from acetic acid solutions. CoS has the same solubilities as NiS.

ZnS, white, from acetic acid solutions; readily soluble in HCl.

Sulphur, white to yellow, from acid solutions of ferric

salts with a simultaneous reduction of the iron to the ferrous state.

H_2S does not precipitate the other members of the group in acid solutions.

Na_2HPO_4 Precipitates:

$CoHPO_4$, reddish to violet blue, soluble in acids and in NH_4OH.

$NiHPO_4$ or $Ni_3(PO_4)_2$, light green, soluble in acids and in NH_4OH.

$FeHPO_4$ or $Fe_3(PO_4)_2$, light green from ferrous solutions; readily soluble in acids. *but acetic*

$FePO_4$, yellowish white, from ferric solutions; soluble in mineral acids; insoluble in fixed alkalies.

$AlPO_4$, white; soluble in mineral acids and in fixed alkalies.

$CrPO_4$, green; decomposed by boiling KOH, leaving potassium phosphate and potassium chromite in solution.

$Mn_3(PO_4)_2$, white; soluble in dilute acids. Turns brown in the air.

$Zn_3(PO_4)_2$, white; soluble in ammonia and dilute acids.

$TiOHPO_4$, white; soluble in mineral acids; insoluble in acetic acid.

KCNS Forms:

$Fe(CNS)_3$, a blood red solution, characteristic of ferric salts in acid solution. Shaking with ether causes the sulphocyanate to go into the ether layer, imparting a deep red color to the ether.

Complex salts of cobalt in concentrated solutions having a deep blue color. The sulphocyanate of cobalt is soluble in ether. When the aqueous solution is shaken with ether a deep blue color is imparted to the ether layer.

$K_4Fe(CN)_6$ Precipitates:

$Co_2Fe(CN)_6$, gray green; insoluble in acids.

$Ni_2Fe(CN)_6$, light green; insoluble in acids; soluble in ammonia.

$Fe_2Fe(CN)_6$ or $FeK_2Fe(CN)_6$, white with ferrous iron; gradually becoming blue due to oxidation; insoluble in acids; transposed by alkalies.

$Fe_4[Fe(CN)_6]_3$, deep blue, called "Prussian Blue," with ferric iron; insoluble in acids, decomposed by alkalies.

$Mn_2Fe(CN)_6$, white, soluble in HCl.

$Zn_2Fe(CN)_6$, white, insoluble in HCl.

Potassium ferrocyanide gives a brown precipitate in lightly acid solutions containing titanium.

$K_3Fe(CN)_6$ Precipitates:

$Co_3[Fe(CN)_6]_2$, red; insoluble in acids. If ammonium chloride and ammonia are added with the ferricyanide a blood red color is obtained.

$Ni_3[Fe(CN)_6]_2$, olive brown; insoluble in acids; transposed by alkalies; soluble in ammonia, forming a green solution.

$Fe_3[Fe(CN)_6]_2$, dark blue, "Turnbull's Blue," from dilute ferrous solutions; insoluble in acids; transposed by alkalies.

$Mn_3[Fe(CN)_6]_2$, brown, insoluble in acids; if an alkali is present the ferricyanide oxidizes the manganese to manganese dioxide, simultaneously forming potassium ferrocyanide.

$Zn_3[Fe(CN)_6]_2$, yellowish, soluble in acids.

Potassium ferricyanide gives a brownish green solution when added to ferric salts in solution.

This reagent gives no reactions with acid solutions of aluminum, chromium and titanium.

Treatment with Suspended BaCO₃ or ZnO:

A thick emulsion of suspended $BaCO_3$ in water when added to cold neutral or lightly acid solutions of the members of the group, precipitates the hydroxides of chromium, ferric iron, aluminum and titanium, but not nickel, cobalt, ferrous iron, manganese, and zinc, the reactions liberating CO_2.

ZnO emulsion added in the cold also precipitates the hydroxides of chromium, ferric iron, aluminum and titanium, but not nickel, cobalt, ferrous iron, manganese and zinc. *ammonium acetate*

$NH_4C_2H_3O_2$ or $NaC_2H_3O_2$ produces:

A deep red color, $Fe(C_2H_3O_2)_3$, when added to ferric salt solutions in the cold. Heating to boiling causes hydrolysis, yielding $Fe(OH)_2C_2H_3O_2$.[1]

A soluble $Al(C_2H_3O_2)_3$ with aluminum salts in the cold, but when heated to boiling $Al(OH)_2C_2H_3O_2$ precipitates. However, if the solution is allowed to cool the basic acetate has a tendency to redissolve, hence the reaction is decidedly reversible, the completeness of conversion depending upon dilution and temperature.

No precipitate with titanium while the solution is cold. However, warming the solution causes hydrolysis of the titanium, causing $TiO(OH)_2$[1] to precipitate completely with sufficient boiling. The titanium can be precipitated completely from 7% to 11% acetic acid solutions, thus differing from aluminum, which can not. If iron is reduced to the ferrous state by SO_2 or sulphites, H_2S,

[1] Even the iron salts of strong acids when largely diluted give insoluble basic salts when boiled. Ferric sulphate when thus treated gives insoluble $Fe_2O(SO_4)_2$, but the action is reversible. A similar hydrolysis occurs with titanium sulphate precipitating $TiO(OH)_2$. With a concentration of less than 3% sulphuric acid the precipitation of titanium is practically complete on long boiling.

etc., boiling its 7% acetic acid solution likewise produces no precipitate. Consequently the above treatment gives a separation of titanium from aluminum and iron.

No precipitation cold or hot with pure chromium salts. However, when considerable iron or aluminum is present the chromium is likewise precipitated to a greater or less extent—sometimes completely. If the chromium is the larger in amount it prevents all the iron and aluminum from precipitating; hence when chromium is present the basic acetate separation is unsatisfactory.

No precipitation with manganous, nickel, cobalt, and zinc salts.

Separation of Phosphoric Acid from Metals by Acetate Hydrolysis:

To a solution containing a few cubic centimeters of H_3PO_4 and a cubic centimeter of a manganese or zinc solution, add NH_4OH till just alkaline, then make acid with acetic, add 5 cc. of $NH_4C_2H_3O_2$ (50% strength) and then $FeCl_3$ till a brownish red color is produced. Dilute and boil. $FePO_4$ is precipitated by this treatment and the first drop of $FeCl_3$ in excess of the quantity necessary to combine with the phosphate will give the deep red color due to the formation of $Fe(C_2H_3O_2)_3$. Upon boiling the excess of iron is precipitated as $Fe(C_2H_3O_2)$ $(OH)_2$. After all the iron is precipitated and filtered out, test the filtrate for the presence of manganese or zinc by making ammoniacal and adding $(NH_4)_2S$.

Under the conditions mentioned above the iron has a greater affinity for the phosphoric acid than any other element of the group, hence the phosphoric acid can be removed from the other elements, especially zinc and manganese, in this way. All the phosphates of the members of this group and barium, strontium, calcium and

magnesium are insoluble in ammoniacal solutions, hence in order to obtain an ammoniacal solution of such of the elements as will remain in ammoniacal solutions the phosphoric acid must be removed.

Oxidation and Reduction:

Cobaltous salts warmed with solid $NaHCO_3$ and H_2O_2 are oxidized to an unstable green compound (probably Na_2CoO_4), the color being more readily detected after filtration. This is a delicate test for cobalt, not being affected by the presence of nickel unless the nickel is in extremely large excess.

See oxidation of nickel and cobalt by bromine water under NaOH and KOH treatment.

Ferrous salts in solution are oxidized by such agents as chlorine water, $KMnO_4$, $K_2Cr_2O_7$, $KClO_3$ and HCl, HNO_3, etc., to the ferric condition.

Manganese compounds are oxidized by fusion with Na_2CO_3 and KNO_3 to Na_2MnO_4, green. Manganese solutions (see note) boiled with PbO_2 and dilute H_2SO_4 (1-2) are oxidized to $HMnO_4$, pink or purple. The color is best seen after the $PbSO_4$ and excess of PbO_2 have been allowed to settle or filtered from the solution. (If a chloride or HCl is present in any considerable quantity in the manganese compound it should be removed by adding H_2SO_4 to the dry substance to be tested and heating till SO_3 fumes appear, then cautiously diluting when cold before the PbO_2 test is applied.)

Chromium compounds oxidize when fused with KNO_3 and Na_2CO_3 to Na_2CrO_4, yellow. If the fused mass is dissolved in water and the solution acidified with acetic acid, the addition of lead acetate precipitates $PbCrO_4$, yellow, soluble in considerable NaOH, forming $Pb(ONa)_2$. H_2O_2 oxidizes a hot solution of $Cr(OK)_3$ or $Cr(ONa)_3$

$$Pb\, ac_2 + H_2CO_3 = Pb\, CO_3 + 2\, Nac$$
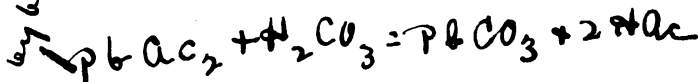
to K_2CrO_4 or Na_2CrO_4. When H_2SO_4 is present H_2O_2 oxidizes a chromate probably to perchromic acid, $HCrO_4$, which imparts a blue color to the liquid. An excess of H_2O_2 reduces the perchromic acid to chromium sulphate, the tendency increasing with the amount of free acid present.

Titanium compounds in acid solution give a yellow or red coloration (TiO_3?) with H_2O_2, persulphates, etc., the depth of color depending upon the amount of titanium present.

Oxalic acid, hydrogen sulphide, sulphurous acid (use a crystal of sodium sulphite), *stannous chloride, potassium iodide*, etc., in the presence of inorganic acids such as HCl or H_2SO_4 reduce the members of this group to lower stages of oxidation in the cold or on boiling. These reactions are shown by using one of the above reducing agents with the solutions of the substances listed below and noting the color change.

$KMnO_4$, pink to purple; changes to $MnSO_4$ or $MnCl_2$, colorless.

$FeCl_3$, yellow; changes to $FeCl_2$ or $FeSO_4$, colorless, or slightly green.

K_2CrO_4 or $K_2Cr_2O_7$, yellow or reddish yellow; changes to $CrCl_3$ or $Cr_2(SO_4)_3$, green.

Cobalt compounds give a characteristic oxidation reaction with KNO_2. KNO_2 added to an acetic acid solution of cobalt and nickel reacts with cobalt, forming $K_3Co(NO_2)_6$, yellow; somewhat soluble in water, but difficultly soluble in solutions containing an excess of KNO_2. Nickelous salts are not oxidized by KNO_2 or HNO_2 and are not precipitated except in very concentrated solutions, when $K_4Ni(NO_2)_6$, dark yellow to red, may form.

Nickel Compounds are precipitated, as $Ni(OH)_3$, by

NaBrO from cyanide solutions, while cobalt remains in solution. KCN solution is added, a few drops at a time, to the *neutral* solution containing cobalt and nickel until any precipitate which forms at first just redissolves, then *2 drops* more are added in excess. The solution is boiled two or three minutes and any residue that remains is filtered off. NaBrO solution is made by adding Br water to 50 cc. of NaOH solution until the solution has a deep yellow color.) The NaBrO solution is poured into the filtrate, and the solution allowed to stand 10 or 15 minutes. After filtration the precipitate is tested with the borax bead. Note: KCN first forms $Ni(CN)_2$, green, and $Co(CN)_2$, brown, which dissolve in an excess of reagent forming soluble $K_2Ni(CN)_4$ and $K_4Co(CN)_6$. On boiling oxygen from the air oxidizes the cobalt to $K_3Co(CN)_6$. The NaBrO oxidizes the KCN first to KCNO and then the nickel to the nickelic state, causing the precipitation of $Ni(OH)_3$, black. Cobalt is not precipitated under these conditions. *Precaution:* KCN can not be added to an acid solution, as HCN, a deadly poison, is evolved. The above solution must be neutral.

Color of the Borax Beads:

OXIDIZING FLAME.	REDUCING FLAME.	METAL INDICATED.
Red Brown	Gray	Nickel
Blue	Blue	Cobalt
Yellow	Bottle Green	Iron
Colorless	Colorless	Aluminum
Colorless	Colorless	Titanium
Colorless	Colorless	Zinc
Yellow-green	Green	Chromium
Violet	Colorless	Manganese

Heated alone on Charcoal.   (If metallic.)

Oxidizes to red oxide in oxidizing flame (Fe_2O_3).   Iron.

Oxidizes to black oxide in reducing filame (Fe_3O_4). Iron.

Oxidizes with incandescent light to white oxide (Al_2O_3). Aluminum.

Oxidizes to white oxide (ZnO, TiO_2), yellow while hot, white when cold.   Zinc, Titanium.

Yields a black oxide (NiO, CoO).   Nickel, cobalt.

Yields a brown to black oxide (Mn_3O_4, MnO_2).   Manganese.

Very slowly yields a green oxide (Cr_2O_3).   Chromium.

Heated alone on Charcoal. (*Salts* which yield oxides, as acetates, nitrates, etc., give the same colors of oxides as noted above.)

The oxides of aluminum and zinc give characteristic colors when moistened with cobalt nitrate and heated.

Blue mass..................aluminum
Green mass.................zinc
Pink mass..................magnesium

Heated on Charcoal with Sodium Carbonate.   Dark, malleable magnetic particles (not globules) are given with iron, cobalt, nickel.

Heated in a Crucible (platinum preferred) with sodium carbonate and potassium nitrate and extracted with water gives:

A red residue (Fe_2O_3).   Iron.

A black residue (CoO, NiO).   Cobalt or nickel.

A white residue (Al_2O_3), (ZnO).   Aluminum, Zinc.

A yellow solution (Na_2CrO_4).   Chromium.

A green solution (Na_2MnO_4).   Manganese.

A white residue (Na_2TiO_3 or unaffected TiO_2).   Titanium.   (See also oxidation and reduction.)

1. (a) Enumerate three tests for ferrous iron, three for ferric. (b) How can you test for ferrous and ferric iron in the presence of each other?

2. Give two good tests for nickel and cobalt.

3. Given the following combinations in solution:

        (a) $MnCl_2$ and $AlCl_3$,
        (b) $KMnO_4$ and $FeCl_3$,
        (c) $NiSO_4$ and $ZnSO_4$,
        (d) $CoCl_2$ and $CrCl_3$,
        (e) $HgNO_3$ and $Fe(NO_3)_3$,
        (f) $CdCl_2$ and $NiCl_2$,
        (g) $SnCl_2$ and $AlCl_3$,
        (h) Ag_2SO_4 and $MnSO_4$,

how can you separate and identify each metallic element?

4. Make a list of all the sulphides and hydroxides precipitated by $(NH_4)_2S$, giving the color of each. How many of these belong to the so-called ammonium sulphide group?

5. What happens when $(NH_4)_2S$ is added to a solution of Na_2CrO_4? Explain.

6. What separation of iron and aluminum could be used based on the solubility of the hydroxides?

7. What elements of this group give characteristic colored borax beads?

8. When H_2S is passed through a solution of $FeCl_3$ the color fades and sulphur is precipitated. Explain in terms of the ions involved.

9. How can you distinguish between ZnO and Al_2O_3 quickly?

10. (a) How can a sulphide separation of nickel and

zinc be made? (b) How can an alkali separation of the same elements be made?

11. Given chromium, aluminum, nickel and iron in a chloride solution, how would you prove quickly the presence of the chromium?

12. Enumerate five separations of different elements of this group from different elements of the first and second groups based upon the use of NaOH, Na_2O_2 or both.

13. Give tests for manganese in the presence of chromium and chromium in the presence of manganese.

14. Give a method of detection of chromic acid (H_2CrO_4) in the presence of chromic chloride ($CrCl_3$).

15. Give a test for nickel in the presence of iron; for iron in the presence of nickel.

16. Write formulas of compounds containing the elements of this group illustrating the lowest and highest valence of each element. Under what conditions are the compounds enumerated stable? Under what conditions unstable?

17. Give a separation and identification of titanium in the presence of (a) iron, (b) chromium, (c) aluminum.

18. How can phosphoric acid be separated from (a) nickel, (b) silver, (c) lead, and (d) zinc?

CHAPTER VIII

THE BASES

Ammonium Carbonate Group, Including Magnesium and the Alkalies

GROUP IV

REACTIONS of solutions of barium, strontium, calcium, and magnesium having a valence of two and sodium, potassium, lithium and ammonium having the valence of one. Use the chlorides or nitrates for the preliminary tests.

Na_2CO_3 or $(NH_4)_2CO_3$ Precipitates:

$BaCO_3$, white; flocculent at first, from neutral or alkaline solutions. This precipitate becomes crystalline when warmed, the change occurring more quickly in dilute solutions. $BaCO_3$ is soluble in HCl or $HC_2H_3O_2$ with effervescence.

$SrCO_3$, resembling $BaCO_3$ in appearance and chemical reactions.

$CaCO_3$, resembling $BaCO_3$ in appearance and chemical reactions.

$Mg_4(CO_3)_3(OH)_2$, white basic carbonate; soluble in large excess of concentrated reagent. From solutions containing magnesium ammonium double salts, as $MgCl_2 \cdot 2NH_4Cl$, magnesium is not precipitated by ammonium carbonate.

Li_2CO_3, white, from concentrated solutions. Considerable alkali chloride or ammonium chloride prevents precipitation.

H_2SO_4 or a Solution of a Soluble Alkali Sulphate Precipitates:

$BaSO_4$, white, finely divided; almost insoluble in water (1 part in about 400,000 parts in water), acids or alkalies.

$SrSO_4$, resembling $BaSO_4$, but more soluble in water (1 part in about 7,000). $SrSO_4$ is more soluble in HCl, hence can not be precipitated so completely from a solution containing HCl as from a neutral solution. $CaSO_4$ although but slightly soluble in water is more so than $SrSO_4$ and hence a saturated solution of $CaSO_4$ will precipitate $SrSO_4$ from a concentrated solution of strontium salt. Precipitation is more complete when the mixture is warmed with a solution of K_2SO_4 or $(NH_4)_2SO_4$ instead of $CaSO_4$. A strong solution of $SrSO_4$ will precipitate $BaSO_4$ for the same reason that $CaSO_4$ solution will precipitate $SrSO_4$.

$CaSO_4$, resembling the barium and strontium sulphates, only from concentrated solutions and then but partially owing to its solubility in water (1 part in 500). A solution of $CaSO_4$ will precipitate $BaSO_4$ and $SrSO_4$ from barium and strontium salt solutions.

H_2SO_4 or a soluble sulphate will *not* precipitate magnesium from solutions of its salts.

K_2CrO_4:

Precipitates from neutral or faintly $HC_2H_3O_2$ solutions, $BaCrO_4$, yellow, almost insoluble in water, soluble in $HC_2H_3O_2$ or HCl.

Does not precipitate $SrCrO_4$ from dilute solutions, neutral or acidified with $HC_2H_3O_2$. $SrCrO_4$ is more soluble in water and acids than $BaCrO_4$. $SrCrO_4$ is precipitated on the addition of alcohol because it is insoluble in alcohol.

Does not precipitate $CaCrO_4$ from neutral or dilute $HC_2H_3O_2$ solutions, because of its great solubility in water. $CaCrO_4$ is not precipitated on the addition of alcohol.

Does not precipitate $MgCrO_4$ for the same reason as $CaCrO_4$.

Na_2HPO_4 or $NaNH_4HPO_4$ Precipitates:

$Ba_3(PO_4)_2$ or $BaHPO_4$, from faintly alkaline or neutral solutions, white, flocculent; easily soluble in HCl, HNO_3, or $HC_2H_3O_2$.

The solubility of the phosphates in acetic acid distinguishes barium from aluminum and ferric iron.

$Sr_3(PO_4)_2$ or $SrHPO_4$, similar to the above.

$Ca_3(PO_4)_2$ or $CaHPO_4$, similar to the above.

$Mg_3(PO_4)_2$ or $MgHPO_4$, white flocculent, like those of barium. From solutions of double salts, like $MgCl_2 \cdot 2NH_4Cl$ in the presence of NH_4OH an alkali phosphate precipitates $MgNH_4PO_4$, white, crystalline; somewhat soluble in water, soluble in acids, nearly insoluble in NH_4OH. The crystalline appearance is most readily apparent when the precipitation is hastened from dilute solutions by stirring with a glass rod.

Li_3PO_4, from moderately concentrated solutions on boiling, white.

$(NH_4)_2C_2O_4$ Precipitates:

BaC_2O_4, white, from concentrated solutions; soluble in HNO_3, HCl or hot $HC_2H_3O_2$.

SrC_2O_4, white; soluble in HCl and HNO_3, soluble with difficulty in $HC_2H_3O_2$. Strontium oxalate is more insoluble than barium oxalate, but much more soluble than calcium oxalate.

CaC_2O_4, white, crystalline; insoluble in water; soluble in HCl or HNO_3; nearly insoluble in $HC_2H_3O_2$; especially insoluble in ammoniacal solutions.

Magnesium does not precipitate, but forms soluble double salts, as $MgC_2O_4 \cdot (NH_4)_2C_2O_4$.

Solubility of Sodium, Potassium, Lithium and Ammonium Salts

The carbonates, sulphates, chromates, phosphates and oxalates of sodium, potassium, lithium and ammonium are all soluble in water. Lithium carbonate and phosphate are difficultly soluble. (See carbonate and phosphate reactions.)

Flame Tests (using preferably the chlorides):

Barium salts when volatilized color the flame green.

Strontium salts impart to the flame a very characteristic deep red color.

Calcium salts tinge the flame a yellowish red.

Magnesium salts do not give a marked colored flame.

Ammonium compounds give no characteristic flame, but the ammonium compounds are very volatile when heated in a porcelain evaporator over the Bunsen flame, the substance appearing like a white cloud.

Potassium colors the flame a deep violet when the potassium salt is introduced by means of a platinum wire into the Bunsen flame. The flame is best observed through a sufficiently thick cobalt blue glass, the sodium rays being absorbed while the potassium rays pass through and are easily recognized. Potassium salts are but slightly volatilized when heated in a porcelain evaporator, unless an intense heat is employed.

Lithium salts color the flame a carmine red similar to the strontium color. In the presence of considerable sodium the red color is masked, hence the cobalt glass is used as in the potassium test.

Sodium gives a brilliant yellow flame when introduced into the flame of a Bunsen burner by means of a plat-

inum wire.   Sodium salts are but slightly volatile when heated in a porcelian evaporator, unless heated very intensely.

Emission Spectra

An examination of the colored flame by means of a spectroscope should always accompany the flame tests. In testing unknown substances the lines observed should be compared with the lines obtained by the use of a pure salt to see if the positions occupied by the lines of the substance tested and the pure salt are identical.

Barium gives a number of lines, some in the orange, more in the green portion of the spectrum.

Strontium gives a number of red lines and a blue line.

Calcium gives several lines in the orange and yellow, one in the green and one in the ultra violet.   The strongest lines are the orange and green lines, which are especially bright.

Potassium gives a very bright red line and two faint lines in the violet.

Sodium gives an intense yellow line, which shows double when a high-grade spectroscope is used.   This line may be observed when only 1 part of sodium is present in about 10,000,000,000, hence must be used with care. Practically all inorganic salts give this line, inasmuch as they are contaminated with sodium to at least this amount.

Lithium gives a bright crimson line between the sodium and potassium lines.

Ammonium salts give no spectrum characteristic of NH_4.

KOH or NaOH Precipitates:

$Ba(OH)_2$, white, voluminous, from concentrated solutions.

$Sr(OH)_2$, like $Ba(OH)_2$, but less soluble in water.
$Ca(OH)_2$, like $Sr(OH)_2$, but less soluble in water.
$Mg(OH)_2$, almost insoluble in water.

KOH or NaOH, when added to a solution of an ammonium salt and the solution warmed, liberates NH_3 gas, which can be detected by moistened red litmus.

NH_4OH Precipitates:

$Mg(OH)_2$ in the absence of sufficient ammonium salts to keep the magnesium in solution. From neutral solutions containing no ammonium salts one half the magnesium precipitates as the hydroxide and the other half remains in solution as double ammonium salt, as $MgCl_2 \cdot 2NH_4Cl$. Barium, strontium, and calcium are not precipitated by ammonium hydroxide.

Solubility in Alcohol and Alcohol-Ether.

Absolute alcohol or a mixture of equal parts of absolute alcohol and ether dissolves both the nitrate and chloride of calcium.

Absolute alcohol or alcohol-ether mixture dissolves strontium chloride but not the nitrate.

Absolute alcohol or alcohol-ether mixture dissolves neither barium nitrate nor chloride.

Sodium and potassium chlorides and nitrates are practically insoluble in solvents of the character of alcohol, alcohol-ether, amyl alcohol, pyridine, acetone, etc.

Lithium chloride has a marked solubility in such solvents as alcohol, amyl alcohol, pyridine, acetone, etc. Ethyl alcohol, amyl alcohol and pyridine are used to separate sodium from lithium, utilizing the varying solubilities of their chlorides in these solvents.

$H_2S, (NH_4)_2S$, and HCl:

Produce no precipitation with members of this group in dilute solution.

Special Tests for the Alkalies.

H_2PtCl_6 Precipitates:

$(NH_4)_2PtCl_6$, yellow, from moderately concentrated solutions of ammonium salts; more insoluble in alcohol and in acetone than in water. Upon ignition the compound is decomposed, leaving metallic platinum as a residue.

K_2PtCl_6, yellow, from moderately concentrated solutions of potassium salts; more insoluble in alcohol and acetone than in water; decomposed on ignition, leaving KCl and metallic platinum as a residue.

Na_2PtCl_6 and Li_2PtCl_6 are soluble in water and in alcohol and acetone, hence are not precipitated by the above reagent.

Fixed Alkalies Liberate Ammonia.

Ammonia Gas, NH_3, is liberated when NaOH or KOH is warmed with an ammonium salt either in solid form or in solution. NH_3 turns moist red litmus paper blue and moist turmeric paper brown. It has a very characteristic odor.

$Co(NO_2)_3 \cdot 3NaNO_2$ Precipitates:

$Co(NO_2)_3 \cdot 3NH_4NO_2$, yellow powder, from acetic acid solutions of ammonium salts.

$Co(NO_2)_3 \cdot 3KNO_2$, yellow powder, from a concentrated solution of a potassium salt containing free acetic but no free inorganic acid. If the potassium salt is acid it should be neutralized with Na_2CO_3 and then acidified with $HC_2H_3O_2$; if alkaline made acid with $HC_2H_3O_2$ before adding the precipitant.

Nothing from sodium or lithium salt solutions.

$H_2C_4H_4O_6$ Precipitates:

$KHC_4H_4O_6$, white, crystalline, from not too dilute solutions of potassium salts. Rubbing the sides of the glass vessel with a stirring rod hastens precipitation. Potassium acid tartrate is readily soluble in mineral acids, soluble with difficulty in water and in acetic acid. If a mineral acid solution is to be tested sodium acetate is added because this salt reacts with the mineral acid giving an acetic acid solution for testing.

$NH_4HC_4H_4O_6$, with chemical and physical properties like the potassium salt.

No sodium or lithium from its salts, the sodium and lithium tartrates being very soluble in water.

H_2SiF_6

Added in excess to a solution containing potassium precipitates K_2SiF_6, white, gelatinous, soluble with difficulty in water, alcohol and dilute acids. Heating the dried salt volatilizes SiF_4, leaving KF.

Does not precipitate ammonium, sodium or lithium fluosilicates from moderately dilute solutions, inasmuch as these salts are soluble in water. They can be precipitated from very concentrated solutions.

$HClO_4$ Precipitates:

$KClO_4$, white, crystalline from not too dilute solutions of potassium salts. The solubility at $0°$ C. is about 1 part in 1200, at $100°$ about 1 part in 5. $KClO_4$ is much more insoluble in alcohol.

NH_4ClO_4, with chemical and physical properties like $KClO_4$, except that it is more soluble.

No sodium or lithium from its salts either in water or alcoholic solution, as the sodium and lithium perchlorates are very soluble in these media.

$K_2H_2Sb_2O_7$ Precipitates:

$Na_2H_2Sb_2O_7$, white, crystalline, from neutral or slightly alkaline concentrated solutions. If the solution is acid neutralize by adding KOH drop by drop.

EXERCISE

1. How many common insoluble sulphates exist?
2. Can you test for strontium in a solution containing all other common elements? How?
3. Give a good test for barium which will apply in hydrochloric acid solution.
4. What would constitute a quick test for magnesium in the presence of barium?
5. How can you test for potassium in the presence of ammonium chloride, using the H_2PtCl_6 reaction?
6. Name a good test for calcium in the presence of magnesium.
7. Name a good test for barium in the presence of calcium.
8. How many sodium compounds can be formed by precipitation? How many of ammonium and potassium?
9. What metals will impart a green color to the flame?
10. How many hydroxides are soluble in water?
11. How many elements will not be precipitated by $(NH_4)_2CO_3$?
12. How many elements precipitate as phosphates from (a) hydrochloric acid solutions, (b) acetic acid solutions, (c) ammoniacal solutions '
13. What other elements besides barium give insoluble chromates in acetic acid solutions?
14. Certain combinations of elements are incompatible. For instance, $SnCl_2$ and $FeCl_3$ can not exist in a stable solution together, as the stannous ch'oride reduces

the ferric chloride, leaving $SnCl_4 + FeCl_2 + FeCl_3$ if the ferric chloride is in excess or $SnCl_2 + SnCl_4 + FeCl_2$ if the stannous chloride is in excess or if in the proper molecular proportions then the resulting solution would be $SnCl_4 + FeCl_2$. State why the following are incompatible: $SnCl_2$ and $KMnO_4$ (in acid solution); $Cu(C_2H_3O_2)_2$ and Na_2S; Na_2SO_4 and $BaCl_2$; $Pb(NO_3)_2$ and K_2CrO_4; $AgNO_3$ and $CaCl_2$. Name five other incompatibles.

CHAPTER IX

THE ACIDS

The Acid Silver Nitrate Group

GROUP I

THIS group includes hydrochloric (HCl), hydrobromic (HBr), hydriodic (HI), iodic HIO₃), ferrocyanic [H₄Fe(CN)₆], ferricyanic [H₃Fe(CN)₆], hydrocyanic (HCN), sulphocyanic (HCNS) and hydrosulphuric (H₂S) acids. These acids react with silver nitrate in dilute HNO_3 solutions, precipitating the · corresponding silver salts. (Use the alkali salts of each for the preliminary experiments. Read again the remarks at head of Chapter V.)

AgNO₃ Precipitates:

AgCl, white; insoluble in HNO_3; much more soluble in NH_4OH than is AgI or AgBr; soluble in $(NH_4)_2CO_3$ [1]; soluble in silver ammonia solution,[2] from which solutions it is reprecipitated by HNO_3. Zinc with H_2SO_4 reduces AgCl to metallic silver.

AgBr, light yellow; insoluble in HNO_3; soluble with difficulty in cold NH_4OH; insoluble in cold $(NH_4)_2CO_3$; practically insoluble in silver ammonia solution. Zinc and H_2SO_4 reduce AgBr to metallic silver.

[1] The $(NH)_4CO_3$ must be freshly prepared or CO_2 must be passed through the solution to transpose any decomposed carbonate.

[2] This solution contains 20 gms. of AgNO₃ and 32 gms. of ammonia (125 cc. of ammonium hydroxide, sp. gr. .90) in a litre of water.

AgI, yellow; insoluble in HNO_3; insoluble in cold NH_4OH or $(NH_4)_2CO_3$; slightly soluble in warm NH_4OH. Zinc and H_2SO_4 reduce AgI to metallic silver.

$AgIO_3$, white; practically insoluble in dilute HNO_3; soluble in NH_4OH; decomposed by NH_4Cl, HCl or a mixture of the two forming soluble NH_4IO_3 or HIO_3. Heat changes it to AgI and O_2. Zn and H_2SO_4 reduce $AgIO_3$ to metallic silver, forming HI.

$Ag_4Fe(CN)_6$, white; practically insoluble in dilute HNO_3; practically insoluble in cold NH_4OH; rather slowly decomposed upon addition of NH_4Cl, HCl or a solution containing equal parts of NH_4Cl and dilute HCl, forming soluble $(NH_4)_4Fe(CN)_6$ or $H_4Fe(CN)_6$ and AgCl, insoluble. $Ag_4Fe(CN)_6$ upon being heated to redness decomposes, yielding Ag, FeC_2, N_2 and $(CN)_2$.

$Ag_3Fe(CN)_6$, red brown; nearly insoluble in HNO_3; soluble in cold NH_4OH; decomposed by NH_4Cl and HCl like the ferrocyanide. When heated to redness $Ag_3Fe(CN)_6$ decomposes, yielding metallic silver like the ferrocyanide.

AgCN, white, insoluble in dilute HNO_3; soluble in NH_4OH and $(NH_4)_2CO_3$; soluble in KCN, forming $AgCN \cdot KCN$; decomposed by a mixture of NH_4Cl and HCl   When heated to redness AgCN yields metallic silver and cyanogen.

AgCNS, white; insoluble in dilute HNO_3; slowly soluble in NH_4OH; soluble in excess of KCNS; partially decomposed by a mixture of NH_4Cl and HCl. It yields metallic silver, cyanogen, sulphur and its oxidation products when heated to redness.

Ag_2S, brownish black; insoluble in cold dilute HNO_3, in cold NH_4OH and in KCN. All other silver compounds are soluble in an excess of KCN.

NOTES

1. The solubility of the silver ha ides and cyanide in ammonia and ammonium carbonate is due to the formation of complex salts, such as $2AgCl \cdot 3NH_3$.

2. The student is urged not to think the complex iron cyanides difficult on account of the number of atoms forming these compounds. They are in reality very simple. In ferrocyanic acid, *ferro* is simply an abbreviation for *ferrous;* hence the iron atom has the valence of two. CN in combination with other elements has the valence of one, for example HCN and NaCN. Then the only necessary point to be remembered is that in the ferro and ferri compounds $(CN)_6$ is always present. Naturally then potassium ferrocyanide must contain four atoms of positive nature besides the two positive bonds of the ferrous atom in ferrocyanide, $(Fe(CN)_6{}^{----})$ and the compound is $K_4Fe(CN)_6$. The zinc ferrocyanide would be $Zn_2Fe(CN)_6$. Analogously *ferri* is an abbreviation for *ferric* and in all ferricyanides three bonds positive are united with the ferricyanogen radicle $(Fe(CN)_6{}^{---})$ thus $Na_3Fe(CN)_6$. Ferrous ferricyanide is then $Fe_3(Fe(CN)_6)_2$.

3. Ag_2S is the only silver salt insoluble in KCN, and Ag_2S, AgI and $Ag_4Fe(CN)_6$ the only ones practically insoluble in cold ammonium hydroxide.

BaCl₂ Precipitates: *oxid 9 rdic*

$Ba(IO_3)_2$, white; slightly soluble in cold, readily in hot, water; insoluble in alcohol; readily soluble in cold HCl; soluble in hot HNO_3. Dilute solutions give a precipitate more readily with $Ba(NO_3)_2$. Inasmuch as BaI_2 is soluble in alcohol, this reaction is conclusive for iodate in the presence of iodide. After precipitation of the iodate, the precipitate is dissolved in HCl, reduced with

$K_4Fe(CN)_6$ or other reducing agent and the free iodine identified by CS_2.

Nothing with the other acids of this group.

Ferrous Salts:

(Use $FeSO_4$ [1], adding it to acid solutions.)

Give no reaction with chlorides, bromides, iodides, sulphocyanates or sulphides. Reduce iodates with the liberation of free iodine.

With $K_4Fe(CN)_6$ precipitate $FeK_2Fe(CN)_6$ or $Fe_2Fe(CN)_6$, white; easily oxidized to ferric ferrocyanide, which is blue.

With $K_3Fe(CN)_6$ precipitate $Fe_3[Fe(CN)_6]_2$, dark greenish blue, " Turnbull's Blue "; nearly insoluble in acids, decomposed by alkalies.

Ferric Salts:

(Use $FeCl_3$, adding it to acid solutions.)

Give no reaction with chlorides, iodides, bromides, or cyanides.

With KCNS give a characteristic deep red coloration due to the formation of soluble $Fe(CNS)_3$.

With $K_4Fe(CN)_6$ precipitate $Fe_4[Fe(CN)_6]_3$, deep blue, " Prussian Blue;" nearly insoluble in HCl; decomposed by alkalies.

Give with ferricyanides a dark brown to yellow solution according to the degree of dilution.

Are reduced by H_2S, forming ferrous salts liberating sulphur.

Precipitate from solutions not too dilute $Fe(IO_3)_3$,

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[1] Ferrous solutions have a tendency to oxidize quite rapidly. If the reagent gives a test for ferric iron, dissolve a crystal or two of solid ferrous sulphate or ferrous ammonium sulphate in water and use the fresh solution.

yellowish white; soluble in excess of reagent; decomposed by boiling.

Special Tests

HALOGEN TESTS

Strong oxidizing agents as MnO_2 and $KMnO_4$ in acid solution evolve the halogens as gases having characteristic colors and odors.

Chlorine water acts on HBr or soluble bromides in acid solution liberating *bromine*. If a few drops of CS_2 are shaken with a solution containing free bromine, the latter is extracted and a yellow color is imparted to the CS_2. $K_2Cr_2O_7$ and KNO_2 will not liberate bromine under similar conditions.

Oxidizing agents, as $K_2Cr_2O_7$, KIO_3, $KBrO_3$, $KMnO_4$, KNO_2, or chlorine water will liberate *iodine* from an acid solution of an iodide, the iodine imparting a violet color to CS_2. When chlorine water and a few drops of CS_2 are added to a HNO_3 solution containing a mixture of iodide and bromide, the iodine is liberated first, coloring the CS_2 violet. The gradual addition of more chlorine water with continued shaking oxidizes the iodine to iodic acid and then the bromine present colors the CS_2 yellow.

$K_2S_2O_8$ added to an acetic acid solution of an iodide liberates the iodine, which will impart a violet color to CS_2. If added to a sulphuric acid solution of a bromide, bromine is liberated, which when shaken with CS_2 tinges the latter yellow. If the persulphate is added to the acetic acid solution of the mixture of bromide and iodide and warmed until all the iodine has been expelled, then addition of sulphuric acid and CS_2 to the cold solution will allow a test for bromide. If persulphate is added to the sulphuric acid solution and boiled until the bromine

and iodine have been completely volatilized, then the $AgNO_3$ test for chlorides is applicable as a test when bromides, iodides and chlorides are originally present together.

IODATE TESTS

Iodic acid (or an iodate) quite strongly acidified with HCl or H_2SO_4 liberates free iodine upon addition of a solution of $K_4Fe(CN)_6$. The free iodine imparts a violet color to CS_2 when shaken with the latter. Other reducing agents of the type $FeSO_4$, CuCl, H_3AsO_3, H_2S, etc., also cause the liberation of iodine.

The presence of iodide in iodate is readily ascertained by acidification, which liberates free iodine. An iodate when acidified with acids such as H_2SO_4 and HCl does not give free iodine.

Sodium or potassium iodates when ignited yield alkali iodides, evolving O_2, then give the characteristic tests for iodide.

FERROCYANIDE TESTS

Soluble zinc salts precipitate $Zn_2Fe(CN)_6$, white, insoluble in dilute HCl, from solutions of ferrocyanides. Zinc ferricyanide is soluble in dilute HCl. Soluble copper salts give with ferrocyanides a red brown precipitate of $Cu_2Fe(CN)_6$.

CYANIDE TESTS

If H_2S is passed through a cubic centimeter or two of an ammoniacal solution containing copper (use the special " copper ammonio solution " for the cyanide test) CuS, black, is precipitated, although incompletely, some of the copper remaining in solution tinging the solution a deep greenish blue to brown depending on the concentration. A small quantity of a dilute cyanide solution (a drop or two) will cause the precipitate to dissolve and give a clear solution due to the formation of $KCu(CN)_2$.

Ferrocyanides, ferricyanides, or sulphocyanates in ammoniacal solutions do not interfere, as the CuS is not dissolved by them and the copper salt of each is soluble in NH_4OH. Ferricyanides cause a change of solution color, but the disappearance of the copper sulphide precipitate is sharp.

When a cyanide solution is made alkaline with NaOH and a mixture of ferrous sulphate and ferric chloride added a greenish blue precipitate containing " Prussian Blue " and ferrous and ferric hydroxides forms. The addition of HCl dissolves the hydroxides, but the deep " Prussian Blue " remains. If ferrocyanides or ferricyanides are present the copper sulphide test is used.

(*Caution*, Cyanide solutions are very poisonous. Keep them alkaline, as in acid solution they evolve HCN, a deadly poison.)

If a solution of a soluble cyanide is added to a dilute solution of copper ammonia salt, made by adding ammonia in excess to copper sulphate, the blue color disappears. $KCu(CN)_2$, K_2SO_4, NH_4OH and $(CN)_2$ are the products of the reaction.

NOTE.—Probably some NH_4CNO is also formed, but in writing the equation this may be neglected.

NH_4OH is added to a solution of a cyanide to alkalinity, then a drop or two of yellow ammonium sulphide and the mixture warmed on a water bath until the odor of the sulphide has disappeared. This treatment forms NH_4CNS. The solution is made faintly acid with HCl and $FeCl_3$ added. A blood red color due to the formation of $Fe(CNS)_3$ develops.

Oxidation and Reduction of Cyanides

Ferrocyanides are oxidized easily to ferricyanides in acid solution by such agents as $KMnO_4$, Cl, etc. $KMnO_4$

likewise oxidizes ferrocyanides in KOH solutions to $K_3Fe(CN)_6$.

Ferricyanides are reduced to ferrocyanides in acid solutions by such agents as H_2S, SO_2, KI, etc. Reducing agents as $FeSO_4$ or $MnSO_4$ with KOH boiling or a chromic salt plus an alkali form the ferrocyanide.

Sulphocyanates are oxidized easily to HCN and H_2SO_4 by such agents as $KMnO_4$, Cl, etc., in acid solution. $KMnO_4$ also oxidizes the sulphocyanate to cyanate and sulphate in alkaline solutions.

Hydrocyanic acid is oxidized to cyanogen chloride by chlorine and to cyanogen iodide by iodine. The cyanides are strong reducing agents forming the cyanates and sulphocyanates with oxygen and sulphur respectively.

SULPHIDE TESTS

Fusion of a solid sulphide with a little NaOH in a porcelain crucible or on a porcelain crucible cover forms Na_2S. If this is dissolved in a few drops of water and a drop of the solution placed on a silver coin a brownish black spot of Ag_2S is formed. Oxygen from the air is a factor in this reaction, NaOH being produced again.

Most of the common sulphides are decomposed by warming with HCl or H_2SO_4, evolving H_2S. When the gas comes in contact with lead acetate paper, made by moistening a filter paper with lead acetate, black PbS is formed.

NOTE.—HCl liberates H_2S from sulphides of the alkalies, alkaline earths, magnesium, iron, manganese and zinc easily; moderately readily from lead, tin, cadmium, antimony, bismuth, nickel, and cobalt sulphides; from the other sulphides with considerable difficulty or not at all. The presence of metallic zinc greatly facilitates action.

1. Given a solution which contains HCl, HBr and HI. Making use of the solubility of the silver salts, how can you separate and identify each?

2. How can you separate the halides from the sulphide of silver?

3. By use of what solubility can you separate ferro-, ferri- and normal cyanide from the sulphide, chloride, iodide and bromide, starting with a mixture of the silver salts?

4. Write the formulas for manganous ferricyanide, ferric ferrocyanide and mercurous cyanide.

5. Give three distinctive tests for the presence of ferrocyanide in solution.

6. Give two procedures for detection of free iodine and bromine in solution.

7. How can you detect free chlorine in a solution?

8. Name two tests for sulphide in an unknown.

9. Explain the principle of the H_2S generator.

10. Zinc ferrocyanide is practically insoluble in dilute HCl. Making use of this fact how can you separate the ferro and ferricyanides from the sulphocyanate and normal cyanide?

11. (a) Name three reducing agents which reduce iodates to free iodine; (b) name three oxidizing agents which liberate iodine from an iodide; and state the conditions for the six tests.

12. In the absence of ferro- and ferricyanides, which tests for cyanide and for sulphocyanate are applicable?

13. Give two methods of identifying an iodate in the presence of an iodide.

14. How can the presence of sodium iodide in sodium iodate be proved or disproved?

CHAPTER X

THE ACIDS

The Neutral Silver Nitrate Group

~~Do all not familiar with~~ GROUP II·

THIS group includes chromic and dichromic, oxalic, phosphoric, sulphurous, arsenous, and arsenic acids.[1] These acids differ from those in the preceding group in not being precipitated by $AgNO_3$ from solutions containing a moderate excess of dilute HNO_3, but they are precipitated by means of the same reagent from neutral or very slightly acid solutions.

(Use the sodium or potassium salts for the preliminary reactions.)

$AgNO_3$ Added to a Neutral Solution Precipitates:

(If the solution is quite strongly alkaline, make just acid with dilute HNO_3, using litmus paper as an indicator, then add the $AgNO_3$. Should the acids be used, ammonia should be added just to alkaline reaction, then a drop of dilute HNO_3 or $HC_2H_4O_2$ added to give slight acidity before the silver reagent is added.[2]

[1] Silver nitrate will also precipitate silver tartrate from a solution containing no free tartaric or acetic acids and likewise silver borate can be precipitated from a fairly concentrated neutral solution, but these acids are not tested for in this group and do not interfere in any way.

[2] If the student is not thoroughly accustomed to the 'process of

Ag_3PO_4, yellow, easily soluble in HNO_3 and NH_4OH; transposed by dilute HCl into AgCl and soluble H_3PO_4.

$Ag_2C_2O_4$, white, curdy; easily soluble in HNO_3 and in NH_4OH; dilute HCl transposes it, forming soluble $H_2C_2O_4$ and AgCl.

Ag_2SO_3, white, curdy; easily soluble in HNO_3 and in NH_4OH; soluble in excess of alkali sulphite forming $NaAgSO_3$; decomposes when heated to $100°$; transposed by dilute HCl, forming soluble H_2SO_3 and AgCl. The precipitation of Ag_2SO_3 is not quantitative.

Ag_3AsO_4, dark red brown; easily soluble in HNO_3 and in NH_4OH; transposed into soluble H_3AsO_4 and AgCl by dilute HCl.

Ag_3AsO_3, yellow; easily soluble in HNO_3 and in NH_4OH; transposed into soluble H_3AsO_3 and AgCl by dilute HCl.

Ag_2CrO_4, red; soluble in strong acids and in NH_4OH; transposed by dilute HCl, forming soluble $H_2Cr_2O_7$ and AgCl.

$BaCl_2$ Precipitates:

$BaCrO_4$, yellow, from neutral or acetic acid solutions; soluble in HNO_3 or HCl.

BaC_2O_4, white, from neutral or alkaline solutions, although the precipitation is always incomplete; soluble in HCl, HNO_3, and $HC_2H_3O_2$.

$BaHPO_4$, white, from neutral solutions. In the presence of ammonia $Ba_3(PO_4)_2$, white, is precipitated. Both are easily dissolved by HCl, HNO_3 or $HC_2H_3O_2$. Solubility of the phosphates of barium in acetic acid distin-

neutralization and the obtaining of a solution giving alkaline or just faintly acid reactions, he should become familiar with the process at once.

guishes them from the phosphates of aluminum and fer-
~~ric iron.~~

$BaSO_3$, white, from neutral but not from sulphurous acid solutions; readily soluble in HCl and HNO_3, and slowly in $HC_2H_3O_2$. Boiling the nitric acid solution slowly precipitates the sulphate. Barium sulphate is insoluble in dilute nitric and hydrochloric acids.

$Ba_3(AsO_4)_2$, white, from neutral solutions; soluble in acids inclusive of H_3AsO_4.

Barium chloride does not precipitate the arsenite from neutral or ammoniacal solutions.

$CaCl_2$ Precipitates:

CaC_2O_4, white, crystalline, from neutral, ammoniacal or acetic acid solutions; soluble in HCl or HNO_3. It is the most insoluble oxalate. When a solution containing calcium is added to the filtrate from the barium chloride precipitation and the solution warmed CaC_2O_4 invariably forms. Precipitation from the acetic acid solution is distinctive. The precipitation is greatly facilitated by warming and agitating the solution.

$CaHPO_4$ or $Ca_3(PO_4)_2$, white, having solubilities like *Comp* the barium salt.   *P Loo*

$CaSO_3$, white, from neutral moderately concentrated solutions; readily soluble in sulphurous acid and other acids; much more soluble in water than the barium salt.

$Ca_3(AsO_3)_2$, white, from neutral or ammoniacal solutions; readily soluble in acids.

$Ca_3(AsO_4)_2$ or $CaNH_4AsO_4$, white, from neutral or ammoniacal solutions; soluble in acids.

Calcium chloride does not precipitate the chromate or dichromate from dilute solutions. From very concentrated solutions the normal chromate can be precipitated.

Magnesia Mixture [1] **Precipitates** (from ammoniacal solutions):

MgNH$_4$PO$_4$, white, crystalline; readily soluble in the mineral acids.

MgNH$_4$AsO$_4$, white, crystalline; readily soluble in the mineral acids.

The arsenite is precipitated from solutions not containing ammonia in excess, but it is readily soluble in ammonia. Chromates, oxalates and sulphides are not precipitated under these conditions.

Oxidation and Reduction:

H$_2$C$_2$O$_4$, H$_2$SO$_3$, and H$_3$AsO$_3$ are readily oxidized in hot acid solutions by KMnO$_4$ (bleaching of KMnO$_4$ easily noticed). Such agents as K$_2$Cr$_2$O$_7$, KNO$_2$ and chlorine or bromine water readily oxidize H$_2$SO$_3$ and H$_3$AsO$_3$ to H$_2$SO$_4$ and H$_3$AsO$_4$ respectively in acid solutions.

Na$_2$SO$_3$, FeSO$_4$, etc., reduce H$_2$CrO$_4$ and H$_3$AsO$_4$ by boiling in the presence of HCl or H$_2$SO$_4$ to CrCl$_3$ or Cr$_2$(SO)$_4$)$_3$ and H$_3$AsO$_3$ respectively.[2]

Special Tests:

(NH$_4$)$_2$MoO$_4$, ammonium molybdate, added in considerable excess to a solution containing arsenic or phosphoric acids acidified strongly with HNO$_3$ and warmed (do not heat to a higher degree than you can comfortably hold your hand on the test tube) precipitates ammonium arsenomolybdate, (NH$_4$)$_3$AsO$_4$·12MoO$_3$, or ammonium phosphomolybdate, (NH$_4$)$_3$PO$_4$·12MoO$_3$, the

[1] Magnesia mixture contains magnesium chloride, ammonium chloride and an excess of ammonia. The function of the ammonium chloride is to form MgCl$_2$·2NH$_4$Cl, from which solution NH$_4$OH does not precipitate Mg(OH)$_2$, but gives a clear solution.

[2] See 2nd Group of Bases for more specific reactions of arsenic and 3rd Group for chromium.

latter precipitating at a lower temperature than the former.

Chlorine water oxidizes H_2SO_3 readily to H_2SO_4 in acid solutions. The addition then of $BaCl_2$ precipitates $BaSO_4$, white; insoluble in excess of HCl or HNO_3.

In the presence of H_2SO_4 the sulphuric acid must be first removed before oxidation of the H_2SO_3. This is accomplished by precipitating the H_2SO_4 with $BaCl_2$ in a solution moderately acid with HCl filtering off the $BaSO_4$ through a hardened filter paper, then oxidizing the H_2SO_3 with Cl water in the filtrate and testing again for H_2SO_4. The precipitation of $BaSO_4$ with $BaCl_2$ then proves the original presence of H_2SO_3.

Modified test for arsenous acid: [1] Place a small portion of a solution containing arsenous acid or an arsenite in a test tube, add aluminum turnings and KOH, insert a piece of cotton in tube to dry the arsine AsH_3. Over the mouth of the tube place a piece of filter paper upon which is a crystal of $AgNO_3$. Warm the solution. The crystal turns yellow (due to the formation of $AsAg_3 \cdot 3AgNO_3$) then black, metallic Ag and H_3AsO_3 being formed. Arsenic acid will not give this test.

. 1. Can the acids of Group I be precipitated by $AgNO_3$ from neutral solutions?

2. Tabulate according to color the silver salts of the members of Groups I and II.

3. (a) If to one portion of a neutral solution you add $AgNO_3$ and obtain a brick red precipitate, and to another portion you add $BaCl_2$ and obtain a yellow precipitate, the presence of what acid is indicated? (b) Un-

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[1] See arsenic reactions in Group 2 of the Bases.

der a similar treatment a deep brown precipitate with $AgNO_3$ and a white precipitate with $BaCl_2$ indicate what acid?

4. Enumerate two tests for the presence of chromic acid.

5. Given KI and K_2CrO_4 in solution, how can you identify the presence of the two acid groupings by a single test?

6. Give a means of separating and identifying arsenous and arsenic acids.

7. In the presence of a ferrocyanide how can you test for a phosphate?

8. In the absence of any other reducing agent, what is a test for oxalic acid?

9. Given a chromate and an arsenate in solution, what is a quick test to apply for the former? For the latter?

10. Utilizing the solubility of the barium salts, how can you separate and identify a chromate and a phosphate?

11. How can you separate and identify a sulphide and a sulphite?

12. Give a rapid identification of an iodide and an arsenite in the presence of each other.

13. What happens when an acid solution of arsenous acid is added to an acid solution of iodic acid?

14. How many and what acids of this group liberate iodine from an iodide in acid solution?

15. From the viewpoint of mass action discuss the precipitation of silver chromate by interaction of silver nitrate and sodium chromate.

CHAPTER XI

THE ACIDS

The Third Group of Acids

GROUP III

THIS group includes sulphuric, chloric, bromic, tartaric, nitric, nitrous, acetic, boric, carbonic, manganic, permanganic, silicic, hydrofluoric and hydrosulphuric acids, each being identified by special tests.

Sulphuric Acid or Sulphates:

From a solution of a sulphate $BaCl_2$ precipitates $BaSO_4$, white; insoluble in HCl. Strontium, lead and barium sulphates are decomposed with difficulty by hot Na_2CO_3 solution. In the analysis for the bases if a residue was left after the water and acid treatments, making a fusion with sodium carbonate necessary, the filtrate from the water extraction after fusion should be acidified with HCl and tested for sulphate, as above.

Chloric Acid or Chlorates:

All chlorates are soluble in water, a little free acid being required for the chlorates of mercury, bismuth and tin.

When a crystal of a chlorate is placed in a dry test tube and a few drops of concentrated H_2SO_4 added, an unstable gas, ClO_2, is produced, which explodes with considerable violence when warmed gently over the Bunsen flame. Small quantities of the chlorate should be used

and the experiment should be performed under the hood, the mouth of the test tube directed away from the operator.

When chlorates are heated decomposition takes place, liberating oxygen and chlorides remain, with which after solution in water silver nitrate precipitates AgCl from dilute nitric acid solutions.

Nascent hydrogen or *reducing acids*, as H_2SO_3, change chlorates to chlorides. The reduction with hydrogen and test is conducted thus: To a solution containing a chlorate in a test tube add a piece of granulated zinc and a few drops of dilute H_2SO_4. Aluminum turnings and KOH can also be used for the reduction. Allow the reaction to proceed a few minutes. The solution is decanted into another test tube, diluted with an equal volume of water and a few drops of $AgNO_3$ solution added. A white curdy precipitate, soluble in NH_4OH and reprecipitated by HNO_3 proves the presence of chlorates. In case the alkaline reduction is employed the solution must be made acid with HNO_3 before the addition of the silver reagent to prevent the precipitation of Ag_2O by the alkali.

Bromic Acid or Bromates: *most bromates*

When a crystal of a bromate is treated with a few drops of strong sulphuric acid free bromine is evolved. Dilute sulphuric acid reacting on a bromate in solution gives bromic acid, which gradually decomposes, yielding free bromine.

Heating alkali bromates liberates oxygen, forming the bromides, which after solution in water give insoluble AgBr with $AgNO_3$ in dilute nitric acid solutions. All bromates ignited with Na_2CO_3 are reduced to bromides and after acidification can be tested with $AgNO_3$.

Nascent hydrogen or *reducing acids*, as H_2SO_3, reduce bromates to bromides, the reactions being similar to those for chlorates.

$H_2C_2O_4$ reduces bromic acid to free bromine in dilute solution, only forming HBr in hot concentrated solutions. The bromine is detected by CS_2.

Silver bromate and barium bromate are the most insoluble normal bromates, these being soluble to the extent of 1 part in about 120 of water at ordinary temperature, hence quite concentrated solutions are required for their precipitation. (Note difference from AgBr.)

Acetic Acid or Acetates:

$FeCl_3$ added to a neutral solution of an acetate forms $Fe(C_2H_3O_2)_3$, a deep red solution. When this solution is boiled a red precipitate of $Fe(C_2H_3O_2)(OH)_2$ forms and the solution becomes colorless. The solution must be neutral before the ferric chloride is added, for if the solution is acid, ferric acetate may not be formed; if alkaline, ferric hydroxide will be precipitated.

Concentrated H_2SO_4 added to an acetate liberates acetic acid upon warming. If a little alcohol is added ethyl acetate $C_2H_5(C_2H_3O_2)$ is formed. Both products have characteristic odors. Until one becomes familiar with the ethyl acetate odor, it is well to make a " blank test " by performing the experiment with alcohol and H_2SO_4 without the acetic acid present and noting the difference.

CoS is easily precipitated from acetate solutions. Saturate a solution of sodium acetate in a test tube with H_2S. Add one or two drops of acetic acid to a solution of cobalt nitrate or sulphate in a test tube and saturate it with H_2S, filter if necessary. Add the first solution to the second and an immediate black precipitate of CoS forms.

If oxides of nitrogen or other weak acids except acetic
are present they interfere with this test. To make this
test of general application, the solution to be tested is
acidified with H_2SO_4 and boiled for a moment to remove
oxides of nitrogen, made alkaline with Na_2CO_3 and
$AgNO_3$ added in slight excess to remove the other weak
acids, then heated to boiling and filtered. The excess of
silver is removed from the filtrate by NaCl and filtration.
Saturate the filtrate with H_2S and add the cobalt solution
prepared as above directed.

Boric Acid or Borates:

Concentrated H_2SO_4 when added to a solid bor
an evaporating dish and gently warmed liberate
acid, H_3BO_3. If a few cc. of alcohol, C_2H_5OH, are
just after the H_2SO_4 (a few cc. of alcohol should be
poured into the test tube from the bottle and the con-
tents of the test tube then poured into the evaporator.
Alcohol is inflammable—be careful) and then warmed
the H_3BO_3 combines with the C_2H_5OH and forms a vola-
tile compound $(C_2H_5)_3BO_3$. Upon ignition the charac-
teristic boron green flame is easily discernible. Smaller
amounts of boric acid are more easily detected if a blow-
pipe with the mouthpiece removed is attached to the gas
supply by means of a rubber tube and a fine flame jet
allowed to burn across and a few mm. above the surface
of this mixture. By this means the first ethyl borate
formed tinges the flame. (Barium and copper must be
removed before this test is applied.)

Turmeric paper when dipped into a solution of a
borate acidified with HCl is colored *reddish brown*. The
color is best observed by carefully drying, wrapping the
moist paper around a test tube containing water which
has been heated to boiling. KOH changes the red to a

greenish black color. (Ferric chloride if present interferes with this test.)

Tartaric Acid or Tartrates:

A few drops of copper sulphate solution added to a solution of a tartrate made strongly alkaline with NaOH or Na_2CO_3 and boiled forms a dark blue solution of $Cu(C_4H_4O_6)$. If copper sulphate is added in excess a greenish blue hydroxide or basic carbonate forms which changes to the oxide on boiling. After filtration the solution shows the characteristic blue color of copper tartrate.

Concentrated H_2SO_4 when added to a tartrate and heated causes the solution to darken due to the separation of carbon. An odor of burnt sugar is noticed and SO_2 is evolved.

$KC_2H_3O_2$ (a saturated solution) added to a tartrate solution slightly acid with acetic acid upon stirring and allowing to stand precipitates $KHC_4H_4O_6$, white, crystalline. Potassium acid tartrate is somewhat soluble in water, hence the precipitation is made with a saturated solution of potassium acetate.

Nitric Acid or Nitrates:

Concentrated H_2SO_4 added to a solution containing a nitrate liberates the HNO_3. The HNO_3 reacting with $FeSO_4$ liberates NO, which unites with the excess of $FeSO_4$, forming a brown unstable compound $(FeSO_4)_2NO$, ferrous nitrosyl sulphate. Ferric sulphate is formed as a by-product. The test is best made as follows: To the solution contained in a test tube add dilute H_2SO_4 till acid, followed by a few cc. of $FeSO_4$. Holding the test tube at an angle of about 45 degrees, allow a few cc. of concentrated H_2SO_4 to flow down the side of the tube.

The strong H_2SO_4, being heavier than water, will for the most part form a layer at the bottom. Where the two layers meet a brown ring will be formed. This ring is most pronounced when waved back and forth gently, causing it to gradually permeate the entire solution, if enough nitric acid is present.

Al+NaOH *Reaction: If iodides, bromides, ferri-* or *ferrocyanides* are present the previous tests are not applicable and the following test is applied: To the solution to be examined in a test tube, NaOH is added in excess. Aluminum turnings are then added and solution warmed. Hydrogen is evolved, reducing the nitrate to ammonia, which is given off as a gas. A piece of moist red litmus paper is held above the tube in the vapor given off, not allowing the paper to touch the glass. If the paper turns blue the presence of nitrates is proven. (See nitrous acid.)

Ag_2SO_4 solution added to a solution containing the acids of the first group with the nitrate precipitates out all but the last-named acid and the usual $FeSO_4$ test can then be applied to the filtrate.

Phenolsulphonic Acid added to the extent of a few drops to the residue obtained by evaporation of a nitrate solution and gently heated forms picric acid. Ammonium picrate, a deep yellow solution, forms when NH_4OH is added to the cooled solution.

Nitrous Acid or Nitrites:

Nitrous acid gives the " brown ring " test, the same as does nitric acid with this characteristic difference. The nitrates require a stronger acid for the liberation of the nitrogen acid. Nitrites are readily decomposed by acetic acid, but the nitrates require strong sulphuric. $HC_2H_3O_2$ is added to the solution to be tested and

thoroughly mixed. A concentrated solution of $FeSO_4$ is then cautiously added to the mixture in a test tube in such a way that the solutions do not mix. The brown ring is easily seen at the junction of the two fluids.

KI added to a nitrite solution acidified with acetic acid liberates free iodine, which can be detected by the use of CS_2. If it is desired to make this test without adding the KI direct, the solution can be placed in a small beaker, acidified with acetic acid and a piece of starch potassium iodide paper moistened and placed on the under side of the watch glass. Acidification forms NO and NO_2, the latter coming off as reddish brown fumes, liberating iodine from the KI and tinging the starch blue.

Reducing Agents, as arsenous, sulphurous, hydroferrocyanic or hydriodic acids are readilv oxidized by a nitrite on acidification.

Nitrites are reduced to NH_3 by the $Al+NaOH$ reaction the same as nitrates. Hence the HNO_2 must be removed by boiling with acetic acid before the nitrate reaction is conclusive.

(Nitrous acid is known only in solution.)

Carbonic Acid or Carbonates:

HCl decomposes carbonates (in the case of iron, bismuth, lead, silver, mercurous, or copper carbonates warming is necessary), evolving CO_2. A film of lime-water $Ca(OH)_2$ taken in a loop tube [1] when brought in contact with the gas becomes turbid by the precipitation of $CaCO_3$. CO_2 when evolved in large quantities redissolves the precipitate, forming the soluble

[1] The loop is made by heating a piece of small glass tubing about an inch from one end and turning it back upon itself in the form of a loop about 3 or 4 mm. in diameter.

$Ca(HCO_3)_2$.   The film should be examined shortly after its exposure to the gas.   If the test tube is warmed and concentrated HCl is used, care must be exercised or HCl will be volatilized and the precipitate in the film will be dissolved.

The carbonate may be placed in a test tube, which is closed with a perforated rubber stopper, through which passes a twice bent delivery tube.   The stopper is removed, some dilute HCl added, the stopper inserted again (the test tube warmed if action is slow), and the gas allowed to pass into clear lime-water contained in another test tube.   The reaction proceeds as in previous test, but is more delicate.

Hydrosulphuric Acid or Sulphides:

The sulphide occurs in this group due to the difficulty of decomposition of some sulphides by boiling Na_2CO_3 solution.   See first group for fusion test.

Manganic and Permanganic Acids and their Salts:

Manganic and permanganic acids are extremely unstable, hence are never used except in the form of manganates, as K_2MnO_4, or permanganates, as $KMnO_4$. Solutions of manganates and permanganates decompose upon addition of a strong acid, liberating oxygen and forming manganese salts of the acid added.   The presence of reducing agents, as $H_2C_2O_4$, $FeSO_4$ and H_2SO_3, greatly facilitates reduction to the manganous state by reacting with the oxygen.   If a halogen acid is used (HCl, HBr, HI) the free halogen is liberated.   The presence of manganate and permanganate in compounds is quite rare, but the latter, being an important laboratory reagent, is tested for in this group of acids.

Silicic Acid or Silicates:

Silicates, unless ground extremely fine, give a gritty feeling when a glass stirring rod is scraped over a little of the substance in the bottom of a beaker.

Silicic acid is easily converted to SiO_2 by heating. In the analysis of an unknown some of the original solution is evaporated to dryness or some of the original solid is fused with 5 times its weight of solid Na_2CO_3 in a platinum crucible until the fused mass is quiet. The melt is cooled, extracted with hot water, and the solution filtered. The filtrate is acidified with HCl, evaporated to dryness, heated on a steam bath for thirty minutes. A white residue, insoluble in concentrated HCl, proves the presence of silicic acid or silica.

NOTE.—The silica dissolves in the fused alkali flux, forming Na_2SiO_3. Acids react with the sodium compound, forming H_2SiO_3, which is converted to SiO_2 by heating. The last product is insoluble in concentrated HCl.

Silica, silicic acid or *a silicate* treated in a platinum vessel with HF forms volatile SiF_4. SiF_4 when allowed to come in contact with water forms insoluble H_2SiO_3, hydrated, white, gelatinous and soluble H_2SiF_6. If a platinum wire loop containing a drop of water is introduced in the gas a white cloudiness due to the formation of the insoluble silicic acid is at once evident.

A bead of microcosmic salt, $NaNH_4HPO_4$, on a platinum wire gives on fusion with a small portion of a silicate a skeleton of silica as a residue in the bead.

Hydrofluoric Acid or Fluorides:

Concentrated H_2SO_4 when added to a fluoride-containing substance in a lead dish and warmed gently (not

over 50–60°) for about an hour evolves HF. If a glass plate covered with paraffine and a few marks or letters scratched through with a knife point is allowed to remain over the dish during the time, the HF will attack the glass, forming SiF_4, volatile. When the paraffine is removed the etching effect is easily noticed.

If silicates are present the above test is not applicable, as the HF immediately forms SiF_4 and no etching occurs. One of the two following tests is employed:

The original substance can be fused with Na_2CO_3 in a platinum crucible, using about a half gram of the original and three grams of the flux. The fused mass is extracted with water, filtered, and the silicic acid precipitated by acidifying with acetic acid. After standing for some time, the mixture is filtered and CaF_2 precipitated by the addition of $CaCl_2$ solution to the filtrate. Filter and test this precipitate as above.

An excess of SiO_2, if not already present, can be added to the original substance, thoroughly mixed, and placed in a small Erlenmeyer flask, which is connected to a test tube containing water by means of a rubber stopper and a glass tube. The mixture is treated with 3–5 cc. of concentrated H_2SO_4 and warmed to not over 50–60°. The SiF_4 distils and reacts with the water, forming soluble hydrofluosilicic acid, H_2SiF_6, and a white precipitate of hydrated silicic acid, probably H_4SiO_4.

$CaCl_2$ Precipitates:

$Ca(BO_2)_2$, white; from moderately concentrated solutions; soluble in HCl, HNO_3 and $HC_2H_3O_2$.

$CaC_4H_4O_6$, white; soluble in a cold solution of KOH; soluble in HCl, HNO_3, and $HC_2H_3O_2$.

$CaCO_3$, white, from neutral or alkaline solutions; soluble in HCl, HNO_3, $HC_2H_3O_2$, and H_2CO_3.

$CaSO_4$, from concentrated solutions; slowly soluble in water, HCl and HNO_3.

CaF_2, white; insoluble in dilute $HC_2H_3O_2$, transposed by strong H_2SO_4.

Acetic, chloric, bromic, nitric, nitrous and the manganic acids are not precipitated by calcium chloride.

$BaCl_2$ Precipitates:

$Ba(BO_2)_2$, like the calcium salt.

$BaC_4H_4O_6$, like the calcium salt.

$BaCO_3$, like the calcium salt, but not so soluble in H_2CO_3.

$BaSO_4$, white; insoluble in water and dilute acids.

BaF_2, white; more soluble than the calcium salt.

Barium chloride gives no precipitate with nitric, nitrous, acetic, chloric, bromic, and the manganic acids.

EXERCISE

1. Given a sulphite and a sulphate in solution, how can you separate and identify each?

2. Given a solution of potassium chromate and potassium arsenate, give conclusive tests for both acid radicals.

3. Given AgI and Ag_2CrO_4, give a single treatment to identify both.

4. A solution is furnished you that contains sodium bromide and possibly sodium nitrate. How can you test for the nitrate?

5. Given potassium oxalate and potassium permanganate, how can you identify both quickly?

6. You are furnished a compound that may contain an acetate or a sulphate. Give quickest test for the former.

7. In the presence of what acids will hydrogen sulphide decompose?

8. How many acids react when treated with a strong oxidizing agent?   With a strong reducing agent?

9. If you boil a solution containing a borate with Na_2CO_3, can any element remain in the filtrate which will interfere with either test for boric acid?   Why?

10. How can you test for HNO_2 and HNO_3 in the presence of each other?

11. A solution contains a chloride and a chlorate. How can you detect each?   What ionic changes are involved?

12. How can you separate a sulphate from an acetate? A carbonate from a nitrate?   A fluoride from a chloride?

13. Give a method for the detection of bromides and bromates in the presence of each other.

14. How can you prove the presence of iodate, bromate and chlorate in a mixture of the three?

CHAPTER XII

ANALYSIS OF UNKNOWNS

Preliminary Examination

QUALITATIVE analysis has for its aim not only the purpose of finding out what elements are contained in a substance but should indicate also the relative quantities of the elements found in the unknown. Sometimes the elements present in the largest amounts are of the most importance and again knowledge of the elements present in only small quantities has the greatest value in the particular case. For instance, an iron ore may contain a high per cent of iron oxide, yet contain as minor impurities sulphur, phosphorus, manganese, silica, aluminum, etc. Now if the product is to be applied to certain metallurgical purposes, the identification of the sulphur, phosphorus and manganese is of the utmost importance even if they are present in small amounts. After qualitative examination the analyst should be able to report the material analyzed as " an iron oxide ore containing sulphur, manganese, phosphorus, etc., in small amount." If magnesium carbonate is the substance undergoing analysis and calcium carbonate is found to be present in very small quantity, then the report should be " magnesium carbonate containing a trace of calcium carbonate as impurity."

In order to correlate properly the relative quantities of substances present the analysis should be started with

a definite amount of material (.5 to 1.0 gm.) and then comparison be made of the bulk of precipitates formed, depth of color produced, etc. Constant caution must be used in such comparisons, inasmuch as some precipitates are very compact and others very bulky, some color reactions very delicate, others less so. However, when in doubt one can take varied amounts of a solution which contains a definite amount of active substance and perform the identification reaction with these and then make the comparison more accurately. Such a comparison is only roughly approximate, however.

The entire amount of material should never be used for the first analysis, but only a portion of it, as frequent use will probably be found for portions of the original substance and in many cases perhaps difficulty would be experienced in obtaining more of the same substance.

Preliminary Examination

If the substance is a *liquid* or a solution note the color, examine the flame with and without a spectroscope (IV, V), observe what occurs in the treatment with acids (VI), then proceed directly with the systematic analysis for acids and bases given in the following chapters.

If the substance is a *gas* consult with instructor as to procedure.

If the substance is a *solid* proceed with the preliminary examination here outlined.

Before starting the specific tests the analyst should observe carefully the physical properties of the substance, particularly noticing if it is homogeneous, crystalline, deliquescent or efflorescent, and, likewise, if it appears to be metallic in character or partakes of the nature of a compound. If the material is a solid mass it should be broken apart, if a powder it should be spread out in a

thin layer on a sheet of white paper or on a watch-glass placed above a sheet of white paper, and note taken if several substances can be seen to be present, or if it is uniform in consistency. Non-uniformity may be shown by variances in color, shape of particles, etc. Frequently the individual particles can be separated into those of the same kind. Many times you are familiar with substances of the same general appearance. Make all the notations you can but draw conclusions ery carefully. Sometimes a preliminary examination w be sufficient to identify the substance being analyzed. In any case such an examination gives information which greatly abbreviates future work and should always be made. However, caution should be observed in avoiding premature conclusions.

I. Heating in a Closed Tube

A small test tube or a glass tube closed at one end is utilized for this test. A small portion of the material is placed in a clean, dry tube, care being observed not to leave any of the material adhering to the side walls of the tube. Held in an inclined position the tube is cautiously heated and all possible observations taken of changes occurring: (*a*) change in condition or appearance of assay (both hot and cold); (*b*) formation of gases which collect in or escape from the tube; (*c*) formation of sublimates, which condense on the cold walls of the tube.

(*a*) CHANGE IN APPEARANCE OF ASSAY

The material may fuse. Only substances which melt easily fuse in the closed glass tube by the heat of a Bunsen burner (e.g., Na_2CO_3).

The material may decrepitate. Particles may snap or explode, even break up into a fine powder (e.g., NaCl).

The material may glow or phosphoresce. Upon heating combustion may take place between an oxidizing agent and a reducing agent, (e.g., $C+KClO_3$). If the phenomenon of burning is noticed caution should be observed in the future handling of the substance, especially when heating or grinding it, otherwise an explosion more or less violent may occur. Some substances glow when heated below redness, even showing color, especially in a dark room.

The material may change color. Decomposition especially may cause change of color. Some substances without decomposing have different colors, depending on the temperature; hence observances hot and cold are important.

The following observances are given as illustrative. The substance may be:

Green or *blue*, and after heating become *black*, either when hot or cold: copper, nickel, (cobalt) compounds.

Green or *brown*, becoming *black*, either hot or cold: iron, manganese compounds.

Pink, becoming *black*, both hot and cold: manganese, cobalt compounds.

Red or *yellow*, becoming *black* while hot, and *dark red* when cold: iron compounds.

White or *colorless*, becoming *dark yellow* to *brown* while hot, and *pale yellow* to *white* when cold: lead or bismuth compounds.

White or *colorless*, becoming *yellow* while hot, and *white* when cold: zinc or titanium compounds.

The changes listed above occur when oxides of the metals result from decomposition caused by heating. Naturally the darker colors may entirely mask the lighter colors and not prove the absence of substances which correspond to those colors.

(b) Gases May be Evolved

Oxygen, colorless, odorless, from peroxides, nitrates, chlorates, iodates, bromates, etc. Detected by supporting combustion of a glowing splinter of wood.

Carbon dioxide, colorless, odorless. From carbonates, bicarbonates, organic substances. (See later.) Detected by cloud imparted to a loop tube containing a drop of lime or baryta water.

Carbon monoxide, colorless, odorless, burns with a blue flame. From oxalates.

Sulphur dioxide, colorless, strong pungent odor. From sulphates with reducing agent, thiosulphates, or sulphides with air. Gives acid reaction to moist litmus paper.

Hydrogen sulphide, colorless, characteristic odor, blackens lead acetate paper. From sulphides containing water.

Ammonia, colorless, characteristic odor. From ammonium compounds. Reacts alkaline to moist litmus paper.

Hydrofluoric acid, colorless, pungent odor. From fluorides (especially those containing hydroxyl). Etches the glass, has strong acid reaction toward indicators.

Chlorine, greenish yellow, pungent odor. From such chlorides as copper and iron or chlorides in presence of an oxidizing agent.

Bromine, red, with pungent odor. From bromides in presence of oxidizing agents.

Iodine, violet, often accompanied by crystals of iodine, characteristic odor. From iodides reacting with oxidizing agents.

Cyanogen, characteristic odor, burns with peach blossom colored flame. From cyanides and double cyanides decomposable by heat.

Nitrogen dioxide, red, pungent odor. From nitrates.

Water, colorless, odorless, condensing on cooler portions of tube in form of drops.   Neutral if pure but alkaline due to presence of ammonia or acid due to presence of volatile acids.   Should be tested with litmus paper.

Organic matter in the form of brown smoke accompanied with dark distillation products with empyreumatic odor, carbon separating as a black charred mass.   From organic material.

(c) SUBLIMATES MAY BE FORMED

Sulphur, red to dark yellow liquid while hot, readily volatile, yellow crystalline solid when cold, characteristic odor.   From free sulphur, some sulphides and thiosulphates.

Sulphides of arsenic, red to black liquid, readily volatile while hot, reddish yellow to transparent solid when cold.   From sulphides of arsenic and the sulph-arsenites.

Oxysulphide of antimony, difficultly volatile solid, black while hot, reddish brown when cold.   From sulphides of antimony and the sulphantimonites.

Arsenic, brilliant black solid, frequently gray near assay, both hot and cold.   From elementary arsenic and arsenides.   If tube is broken off below the deposit and then reheated the characteristic odor of garlic is at once evident.

Mercuric sulphide, brilliant black solid, hot or cold.   If the sublimate is removed and rubbed it gives a red powder.

Mercury, minute gray globules, which can be united by rubbing with a glass rod or paper.   From metallic mercury, mercury oxides and amalgams.

Chloride of lead, double chlorides of lead and antimony, mercuric chloride, mercurous chloride (yellow while

hot), ammonium salts, oxides of arsenic and antimony yield white solids. A number of iodides and bromides volatilize also, especially those of mercury, lead and bismuth.

II. Heating on Charcoal

When a small portion of the material being examined is heated on charcoal one may notice characteristic (a) odors; (b) sublimates; (c) formation of metallic globules or magnetic masses; (d) infusible light colored compounds.

(a) ODORS

Sulphur burns when heated on charcoal in the oxidizing flame, giving a blue colored flame and characteristic odor. Sulphides give the same phenomena.

Arsenic and arsenides in the reducing flame give an odor of garlic, the vapors becoming white as the arsenic volatilizes, due to oxidation.

(b) SUBLIMATES

Arsenous Oxide, As_2O_3, white, very volatile, mostly distant from the assay. Frequently the garlic odor is very noticeable. From arsenic, its sulphides, etc., when they are roasted in air.

Oxides of Antimony, Sb_2O_3, Sb_2O_4, dense, white, settling quite near the assay. From antimony, its oxides and sulphides when they are roasted in air.

Zinc oxide, ZnO, near the assay, canary yellow while hot, white when cold; distant from assay faint white. Heating some zinc compounds in the reducing flame forms metallic zinc, which volatilizes, becomes oxide, then condenses on the charcoal. Moistened with cobalt nitrate and again ignited it gives a green coating.

Tin oxide, SnO_2, faint yellow to white when hot, white when cold. Not volatile in oxidizing flame.

Moistened with cobalt nitrate and reignited the coating assumes a bluish green color.

Lead oxide, PbO, dark yellow when hot, sulphur yellow when cold near the assay, blue white distant from assay. Volatile in oxidizing and reducing flames. If coating is moistened with hydriodic acid and heated a volatile yellow green lead iodide forms.

Bismuth Oxide, Bi_2O_3, near assay dark orange yellow while hot, yellow when cold; distant from assay greenish white. Volatile in both oxidizing and reducing flames. Moistened with hydriodic acid and heated forms volatile chocolate brown bismuth iodide.

Cadmium Oxide, CdO, near assay dark brown, almost black, changing to red brown in short distance; distant from assay is yellow. Volatile in both oxidizing and reducing flames.

(c) Metallic Globules or Magnetic Masses

The material is first heated alone on the charcoal and observation taken then Na_2CO_3 added and again heated, using reducing flame in both instances.

Lead, easily fusible, bright lead gray globules in reducing flame, readily malleable, soft, leaves black streak on paper. Heated in oxidizing flame gives coating of yellow oxide.

Bismuth, easily fusible, bright lead gray globules in reducing flame, but brittle. In oxidizing flame yields a yellow oxide.

Tin, easily fusible, bright gray white in reducing flame, but coated with white oxide in oxidizing flame. Metal soft and malleable.

Copper, difficultly fusible, bright red in reducing flame, but oxidizing flame causes it to coat with black oxide. Metal is malleable.

Silver, difficultly fusible, bright white when hot and cold; no oxidation occurs. Metal is malleable.

Globules are frequently obtained which resemble metals, but which are combinations of metals with non-metals, such as sulphur, antimony, or arsenic. These are very brittle and tarnish readily.

Magnetic globules or masses are obtained when iron compounds are heated on charcoal, especially with Na_2CO_3. Nickel and cobalt give such phenomena, but less often.

Alkaline reaction. When no Na_2CO_3 has been used the residue, after ignition, dissolved from the charcoal with a few drops of water often gives an alkaline reaction to turmeric paper, indicating one of the alkalies or alkaline earths.

Sulphur. After fusion with Na_2CO_3 in the reducing flame, a few drops of water added and a drop placed upon a clean, silver coin, a black stain indicates some sulphur containing substance in the unknown.

(d) INFUSIBLE LIGHT COLORED COMPOUNDS

These are tested by the addition of cobalt nitrate after the first ignition, followed by a reignition.

Magnesium oxide, MgO, pale pink, not very easily recognized.

Zinc oxide, ZnO, green, best observed when cold.

Tin oxide, SnO_2, blue green, best applied to a coating.

Aluminum oxide, Al_2O_3, blue, very distinctive except in presence of zinc silicate.

Zinc silicates, blue.

III. Color of Beads on Platinum Wire

(a) Borax Bead.

(b) Sodium Carbonate Bead.

If the substance to be examined is not an oxide it should be roasted on charcoal or in a crucible, as such treatment frequently converts it to the oxide and in such form the tests are more reliable. The colors given are those produced with the pure oxides of the metals enumerated. Mixtures of oxides may give numerous shades and varieties of color. Care should be taken that the wire is clean. If not clean it should be cleansed thoroughly (HCl is usually effective) and finally heated several times with some of the flux to be used and each time the flux shaken off before use in the test.

(a) Borax Bead Tests

Copper, a green color in hot oxidizing flame when the bead is strongly saturated with copper salt and blue when small amounts of copper are present. Colorless to green, except when strongly saturated, when it is red in reducing flame.

Iron, a yellow coloration in the oxidizing flame, and green in the reducing flame.

Chromium, a yellow green coloration in oxidizing flame, and green in reducing flame.

Cobalt, a blue coloration to the bead in hot or cold oxidizing or reducing flames.

Nickel, red brown coloration in oxidizing, and gray opaque in reducing flame.

Manganese, violet to red violet in oxidizing, and colorless in reducing flame.

(b) Sodium Carbonate Bead Tests

Manganese in oxidizing flame, green when hot, blue when cold. Colorless in reducing flame.

Chromium gives a yellow bead in the oxidizing flame.

Silica dissolves in the fusion, yielding a clear glass.

(If a bead of microcosmic salt, $NaNH_4HPO_4$, is substituted for the borax or Na_2CO_3, then after fusion of a silicate in the bead a skeleton of silica is left as residue.)

IV. Flame Coloration

The chlorides, being more volatile than many other compounds, color the flame more readily and are commonly used for the flame tests. Conversion to chlorides is usually accomplished by moistening with hydrochloric acid. The colors enumerated correspond to the pure salts. In the presence of several elements giving color one coloration may mask another partially or completely. The color of the sodium flame is very intense and often obscures all other flame colorations. The violet of the potassium flame is hidden completely in the presence of sodium, but by viewing the flame through a blue glass or indigo solution the yellow rays are absorbed and the violet coloration due to potassium is readily observed.

The platinum wire is fused into a piece of glass tubing to serve as handle. The wire i always cleaned before using by dipping it into a little concentrated hydrochloric acid contained in a watch-glass, then heating the wire. This operation is repeated until the wire gives no flame coloration. The wire is then heated, brought into contact with the substance to be analyzed, heated again and color of flame noted. Often mo stening a small portion of the substance with hydrochloric acid before heating on the wire increases the volatility of the element or elements, hence gives a more distinct flame. The following colors may be noted:

Barium, copper, boric acid, green.
Calcium, orange.
Sodium, yellow.
Potassium, violet.

Lithium, Strontium, red.
Lead, Arsenic, Antimony, light blue.

V. Spectroscopic Examination

See " Emission Spectra " of members of the Ammonium Carbonate Group (page 74).

VI. Treatment with Acids

A small portion of the substance is treated with a small amount of dilute hydrochloric acid in a small test tube, warming, if necessary, and observance taken of (*a*) evolution of gases, (*b*) color of solution, (*c*) appearance of residue. If the action of dilute acid is slow stronger acid is applied.

(*a*) EVOLUTION OF GASES

The odor of the gases should be taken very cautiously, inasmuch as poisonous gases (especially HCN) may be evolved. This test is best performed at the hood.

Hydrogen, colorless, odorless, combustible. From a metal.

Hydrocyanic acid, colorless, characteristic odor, very poisonous. From a cyanide.

Carbon dioxide, colorless, odorless. From a carbonate; detected by bringing in contact with lime or baryta water.

Sulphur dioxide, colorless, characteristic odor. From a *sulphite;* bleaches $KMnO_4$ solution in a loop tube.

Hydrogen sulphide, colorless, characteristic odor. From a sulphide (or a sulphate or sulphite and a strong reducing agent); blackens moist lead acetate paper.

Chlorine, greenish yellow color, characteristic odor. From an oxidizing agent; colors potassium iodide starch paper deep blue (almost black).

Bromine, red color, very penetrating odor. From a bromide and an oxidizing agent; colors potassium iodide starch paper deep blue (almost black).

Iodine, violet vapors, frequently accompanied by separation of iodine crystals on the sides of the test tube, very penetrating odor. From an iodide and an oxidizing agent; colors starch paper deep blue (almost black).

Oxides of nitrogen, brown, characteristic odor. From a nitrate and a reducing agent.

(b) COLOR OF SOLUTION

Ferric iron, yellow to red, due to formation of $FeCl_3$.

Copper, ferrous iron, nickel or *chromium,* green, due to formation of $FeCl_2$, $NiCl_2$, mixture of $CuCl_2$ and $FeCl_3$ or $CrCl_3$.

Copper, greenish blue, due to formation of $CuCl_2$.

Cobalt or *Manganese,* pink, due to formation of $CoCl_2$ or $MnCl_2$.

(c) APPEARANCE OF RESIDUE

Sulphur, white or yellow residue, due to presence of a sulphide and an oxidizing agent, a sulphite and a reducing agent, or a thiosulphate.

Chlorides may be formed which may be soluble or insoluble in water, depending upon the strength of acid used in the test.

Silicic acid, white, may separate in the form of a jelly. From a silicate.

A white residue may be left from a variety of sources, especially from insoluble halides, sulphates, oxides and silicates.

A dark or *black residue* may be left, due to undecomposed metals, alloys, oxides, sulphides, silicates, etc.

If the residue is dark or black, it is treated with concentrated nitric acid. Should sulphur separate the presence of a sulphide is indicated.

VII. Solubility

The solubility from viewpoint of quantity dissolved and color of the extracted solution should be observed for the following solvents:

(*a*) Water;

(*b*) Hydrochloric acid (dilute and concentrated);

(*c*) Nitric acid (dilute and concentrated);

(*d*) Aqua regia.

VIII. Tabulation of Indications

After the preliminary tests are concluded the elements indicated to be present are carefully tabulated. In certain cases conclusions may be drawn as to the exact composition of the material under examination. However, usually the observances should be confirmed by the systematic analysis of the material, recognizing the indications observed.

CHAPTER XIII

PREPARATION OF SOLUTIONS FOR THE DETECTION OF THE BASES AND ANALYSIS OF THE INSOLUBLE RESIDUE FOR BOTH BASES AND ACIDS

Preparation of Solutions for the Detection of the Bases

Three conditions may arise:

(1) The unknown is a liquid or in solution.

(2) The unknown is a solid compound or mixture of compounds.

(3) The unknown is a metal or an alloy.

(1) THE UNKNOWN IS A LIQUID OR IN SOLUTION

If a liquid and not a solution, a portion is poured into water and converted into a solution if possible in this manner. Should a precipitate form, it is treated the same as under (2) The Unknown is a Solid. The solution is treated the same as if it were the original solution.

If a solution, a portion is prepared for the precipitation of the first group and subsequent groups of bases. Ferro- or ferricyanides, oxalates and tartrates interfere, especially in the precipitations with H_2S and $(NH_4)_2S$ and must be removed. Consequently, if any are present the solution is evaporated to dryness and the residue fused with about five times as much NH_4NO_3 in the hood where the draft is good. This treatment decomposes the interfering acids. Cool and extract with dilute nitric acid. Treat any residue remaining according to (2) The Unknown is a

Solid. Analyze the nitric acid solution systematically for the bases, remembering that potassium and iron are present as decomposition products from the cyanides.

If ferro- or ferricyanides are not present the solution is tested for acidity or alkalinity. If acid proceed to test for the presence of group one.

If the solution is alkaline, acidify with HNO_3. Should a precipitate form, dissolve it with a slight excess of HNO_3, warming if necessary; if the residue is insoluble in HNO_3 treat it according to (2) The Unknown is a Solid. The HNO_3 solution is ready for testing for the presence of members of group one and subsequent groups.

(2) The Unknown is a Solid Compóund or a Mixture of Compounds

If ferro- or ferricyanides, oxalates or tartrates have been found in the analysis of the acids fuse .5 to 1.0 gm. cf the unknown with about five times as much NH_4NO_3 to decompose the interfering substances, then proceed to dissolve in the manner given below.

The sample should be uniform and finely divided before using for analysis. If not already so a small portion should be ground in a mortar. If no explosion occurs grind a larger amount for analysis. After grinding the solid is well mixed.

The effect of various solvents is tried in succession with .5 to 1.0 gm. of pulverized material. The order usually observed is (1) hot water, (2) hot dilute HCl, (3) hot dilute HNO_3 and (4) aqua regia. Sometimes concentrated HCl and HNO_3 are more serviceable but the dilute acids should *always* be used first. The solid is boiled with successive small portions of water, until no more will dissolve, filtering after each treatment. The

residue is then boiled with successive small portions of HCl, again filtering after each treatment. The residue from HCl treatment is next treated with HNO_3, etc. Tabulate the solubilities, as they will usually be serviceable in helping you eliminate many of the bases after analysis of the acids.

As complete a separation as is possible is desired by means of each of the solvents. The residue left after each treatment is washed thoroughly with hot water and the first washings added to the filtrate. Should any doubt exist regarding the solubility of the substance in any solvent or the completeness of solution in any particular solvent a little of the filtrate is evaporated to dryness in a porcelain dish. If no residue remains the solution may be discarded and the substance treated with the next solvent in regular order. (A very slight dark residue may be due to dust and may be discarded.)

Water Solution. If any of the substances have dissolved in water test the solution with litmus paper. If it is neutral or acid proceed with the analysis for the bases as directed under " Solutions." If alkaline make slightly acid with HNO_3. If the precipitate formed is soluble (test a small portion) in HNO_3 add sufficient HNO_3 to redissolve it. If the precipitate does not dissolve, filter, wash with water, and treat it as if it were a solid substance insoluble in water. This HNO_3 solution is then analyzed for the bases as directed in " Solutions," page 121.

HCl *Solution.* The residue from hot water treatment is treated with dilute HCl, heating if necessary. Add HCl and boil until no further action is obtained. Indications of the presence of certain acids, Br, I, Cl, CO_2, SO_2, S, etc. (see preliminary examination), may be observed by this treatment. If the treatment

with HCl seems to form insoluble chlorides of first group metals, treat with HNO_3 before HCl. The HCl solution can contain no members of the HCl group, except lead, unless concentrated acid is used, in which case AgCl will dissolve to some extent. Any dissolved silver will be reprecipitated by diluting the solution with three times its volume of water. After the precipitate has been removed by filtration and tested for silver, the analysis should be proceeded with as with the water solution after the precipitation of the HCl group.

HNO_3 *Solution.* Dilute and analyze as in the case of a water solution, removing the nitric acid and converting the nitrates into chlorides by evaporating a couple of times with HCl, then dissolving the substance in water and adding the requisite amount of HCl before treating with H_2S for second group metals. If a sulphide is present that has not been reacted upon by HCl free sulphur will be liberated when treated with HNO_3 or aqua regia.

If the HNO_3 treatment has preceded the treatment with HCl, thus dissolving members of the First Group of Bases, HCl should be added to complete precipitation preceding evaporation. The insoluble chlorides are analyzed for the presence of the first group of bases, and the filtrate evaporated with HCl as above indicated to remove the HNO_3.

Aqua Regia Solution. Boil to expel chlorine, evaporate with HCl to decompose completely any remaining HNO_3, dilute with three times its volume of water to precipitate any first group metals, then proceed with the other groups in regular succession as before.

These Solutions Frequently May Be United. If the union of the water, HCl, HNO_3, and aqua regia solutions causes no precipitation, as ascertained by a prelim-

inary experiment, they may be united and the resulting solution then analyzed for the bases. If a precipitate forms which is soluble in an excess of HCl upon warming, and does not reprecipitate upon cooling (the precipitate of $PbCl_2$ does not interfere), the solutions may be united. If the precipitate is not soluble in HCl, add HCl to the water solution and likewise to the HNO_3 solution and analyze this precipitate for the presence of first group bases. Add the HCl and aqua regia solutions to the combined filtrates of the first two. If no precipitate is produced by this union, boil off HNO_3, displacing it with HCl, and proceed as usual. If a precipitate is produced analyze the solutions separately.

Analysis of the Insoluble Residue for Both Bases and Acids

This residue may contain:

$BaSO_4$, $SrSO_4$, ($CaSO_4$), $PbSO_4$, CaF_2, AgCl, AgBr, AgI, AgCN, (ferro- and ferricyanides), silicon, silicates (which frequently contain HCl, HF, HBO_2, H_2SO_4, H_3PO_4), C, S, SnO_2, TiO_2, Fe_2O_3, Cr_2O_3, Al_2O_3.

The C is detected by burning it to CO_2 and passing the CO_2 into lime or baryta water (see carbonates). The S is recognized by its odor when heated and burning it to SO_2, which is absorbed in bromine water, and adding barium chloride for the sulphate test, thus confirming the original presence of sulphur. Each of these tests can be easily performed by placing the material in a hard glass tube which is connected to a small Drechsel wash bottle containing the bromine-water or lime-water for the test. The tube is supported on two ring stands by means of clamps. Air is drawn through the apparatus by suction and the material in the tube is heated by means of a Bunsen burner. When testing for CO_2 the air must

be purified from CO_2 by passing through a soda lime tube or tower, or through KOH solution before it enters the tube containing the material being tested.

$PbSO_4$ is soluble in a strong solution of ammonium acetate containing a little acetic acid on heating to boiling for a few minutes. After filtration, if solution is not complete, the filtrate is tested for lead and for sulphuric acid (see tests).

The residue from the ammonium acetate extraction may contain undissolved $PbSO_4$, AgCl, AgBr, AgI, etc. A portion of this residue is heated in a porcelain dish with Zn and dilute H_2SO_4 and after filtering off the metallic lead and silver, tested for *halogens* according to procedure F of the First Group of Acids. The metallic residue is dissolved in nitric acid and the solution tested for *silver* according to directions given in the First Group of Bases. The larger portion of the residue is suspended in about 50 cc. of water containing 2 or 3 cc. of ammonia and hydrogen sulphide passed through the mixture for several minutes. After filtration the residue is treated with warm dilute nitric acid to dissolve the sulphides of lead and silver. The residue is again suspended in 50 cc. of water containing 2-3 cc. of ammonia and hydrogen sulphide passed. This alternate treatment with hydrogen sulphide and nitric acid is continued until no black precipitate is obtained with hydrogen sulphide, thus insuring complete removal of the lead and silver salts from the residue.

The residue from the extraction of the silver salts is dried and then one-half of it fused with about 5 to 6 times as much $Na_2CO_3 + K_2CO_3$ in a platinum crucible. The mixture is heated to a good red heat until the fusion is quiet (15-20 min.). $BaSO_4$, $SrSO_4$ and $CaSO_4$ are converted to $BaCO_3$, $SrCO_3$ and $CaCO_3$ respectively and the

soluble alkali sulphates; CaF_2 is converted to $CaCO_3$ and soluble alkali fluoride; silicates are decomposed into insoluble oxides and carbonates of the metals and soluble alkali silicate containing also soluble alkali chlorides, fluorides, borates, sulphates, and phosphates which are present as minor constituents usually; silica dissolves, forming soluble alkali silicates.

The fusion is allowed to cool, thoroughly extracted with hot water and filtered. The residue is dissolved in HCl and tested systematically for the bases, with especial attention to the presence of members of the $(NH_4)_2S$ and $(NH_4)_2CO_3$ groups. (Naturally this residue and likewise solution can not be tested for alkalies due to the previous use of alkali carbonates. See special test for alkalies.) Part of the solution is made acid with HNO_3 (filtering off any silicic acid which may form) and tested for the halogens and phosphoric acid. A portion is made acid with HCl and (a) tested for sulphate, (b) evaporated to dryness and heated to dehydrate the silicic acid, extracted with dilute hydrochloric acid and the residue tested for silica by the HF test. Another portion is acidified with sulphuric acid (filtering off any silicic acid) and tested for (a) boric acid and (b) hydrofluoric acid.

The residue after extraction with HCl may still contain SnO_2, TiO_2, Cr_2O_3, Fe_2O_3 and Al_2O_3. It is fused in a nickel or silver crucible with Na_2O_2. This fusion is best accomplished by using about five times as much fusion material as solid to be fused, heating just sufficiently to melt the Na_2O_2 and insure a uniform mass, then a portion of Na_2O_2 equal to the first is added and the mass heated again. The fusion melt is then cooled and extracted with water, after which the solution is boiled to decompose the excess of Na_2O_2. After filtration the tin, chromium and aluminum are in solution as sodium

stannate, chromate and aluminate. The titanium and iron are in the residue as insoluble sodium titanate and titanium dioxide and ferric oxide with nickel oxide from the crucible, if a nickel vessel is used. The solution is acidified with hydrochloric acid and H_2S passed through the solution to precipitate completely the tin. The filtrate is boiled to expel the H_2S and if yellow before the passage of H_2S it should be made alkaline with NaOH and Na_2O_2 added to reoxidize the chromium to chromate. The solution is then boiled to decompose the excess of Na_2O_2 and reacidified with acetic acid. $BaCl_2$ is added to precipitate the chromate. A yellow precipitate proves the presence of chromium. The filtrate is made just ammoniacal and boiled. A white gelatinous precipitate indicates aluminum. (A crystalline precipitate may form due to absorption of CO_2 from the air and formation of $BaCO_3$.) This precipitate is dried and ignited with cobalt nitrate. A blue mass proves the presence of aluminum. (A blank test should be applied to see how much, if any, aluminum is contained in the Na_2O_2.) Titanium is tested for in the residue by igniting the dried nickel-iron-titanium residue and fusing with about six times as much $KHSO_4$ to a quiet fusion. After cooling the mass is extracted with 10% sulphuric acid in the cold, which dissolves the titanium, iron and nickel as sulphates. The solution is made strongly ammoniacal, boiled and filtered. The $TiO(OH)_2$ and $Fe(OH)_3$ are then dissolved in a minimum amount of hot 1–1 HCl and cooled. After neutralizing, leaving the solution just decidedly acid, it is tested for iron and titanium. To one portion add KCNS. A blood red solution proves the presence of iron. To another portion add about 10 cc. of phosphoric acid, 10 cc. of Na_2HPO_4 solution and 5 cc. of 3% H_2O_2. A yellow to red colora-

tion not bleached by Na_2HPO_4 solution proves the presence of titanium. If a deep color is obtained a third portion should be tested as follows: Add a few cc. of HCl, then solid Na_2SO_3 to the solution until the solution is colorless, heat to boiling for a few minutes. A white flocculent precipitate proves the presence of titanium.

Special Test for Alkalies in a Silicate

The finely ground substance is well mixed with about five to ten times as much of a mixture consisting of $CaCO_3$ and NH_4Cl in the ratio of 8 : 1 and heated slowly in a platinum crucible until the white fumes of NH_4Cl cease coming off, finally increasing the heat to redness for a few minutes. After cooling the mass is extracted with hot water and filtered. The alkalies with calcium are in solution as chlorides. The most of the calcium is precipitated by addition of NH_4OH till alkaline, then $(NH_4)_2CO_3$ and the carbonate filtered off. The filtrate is heated to boiling and $(NH_4)_2C_2O_4$ added to complete precipitation of the calcium. After filtering off the CaC_2O_4 the filtrate is evaporated to dryness and ignited to remove the ammonium salts. The residue is moistened with HCl and again evaporated. The mixed chlorides of the alkalies are now soluble in water and can be tested according to the treatment given in the Fourth Group of Bases ($(NH_4)_2CO_3$ Group).

(3) THE UNKNOWN IS A METAL OR AN ALLOY

The qualitative analysis of a metal or an alloy is much simpler than that of a solid compound or mixture of compounds, inasmuch as certain basic elements do not alloy readily and very few of the electronegative elements

can be present, sulphur, phosphorus, carbon and silicon being the only ones usually considered.

All the common metals except tin and antimony are soluble in nitric acid, hence nitric acid is the best solvent for alloys in general. However, some alloys, especially those high in silicon content, resist the action of all acids. Such alloys are best decomposed by an alkali fusion in a silver crucible,[1] and after decomposition the melt extracted with nitric acid. Hydrochloric acid or similar acids should not be used as a solvent for an unknown alloy, as the non-metallic elements, phosphorus, arsenic, carbon, silicon, sulphur or antimony, may be evolved as their volatile hydrogen compounds.

.5 to 1.0 gm. of the unknown (drillings or chippings preferred) are treated with 10 to 20 cc. of $HNO_3(1-1)$ in a hood where the draft is good, warming if necessary after the first action has subsided. After thorough decomposition, the solution is carefully evaporated almost to dryness. (This is best done on a water or steam bath. If performed over a free flame constant stirring should accompany evaporation to avoid sputtering. When the free flame is used a casserole is preferred as a vessel.) Do not allow the mixture to overheat, otherwise difficultly soluble basic salts may form. Should this happen add a little more concentrated HNO_3 and warm again, add water, evaporate again. Water is then added and the solution warmed.

Two conditions may arise:

(a) A clear solution is obtained with no residue. In such cases the unknown contains no tin or antimony. This solution is analyzed according to the usual

[1] The melt is extracted with water and removed from the crucible preceding the treatment with HNO_3. Naturally a silver crucible will not withstand the action of HNO_3.

scheme of analysis, commencing with Group I of the Bases.

(b) A residue is obtained—white or greenish white. A little of the solution is evaporated to dryness to ascertain if any metal has dissolved. If no residue is obtained the solution may be discarded. If a residue is obtained then proceed with the solution as usual, commencing with Group I of the Bases after including solutions to be mentioned later.

The residue insoluble in HNO_3 may contain SiO_2, Sb_2O_3, Sb_2O_5, SnO_2, Bi_2O_3, P_2O_5 and traces of Cu, Pb, Fe, Mn, etc. This residue is suspended in about 40–50 cc. of water and 5–10 cc. of K_2S solution added and warmed for several minutes (do not boil), then filtered. The residue may contain SiO_2, Bi_2S_3, CuS, PbS, FeS, MnS, etc. The sulphides are dissolved in dilute nitric acid and added to the solution to be tested for the bases previously mentioned or tested separately if there is no such solution. The SiO_2 is tested by treating with HF in platinum and getting the turbidity of silicic acid with a drop of water in a platinum wire loop tube. The solution may contain K_2SnS_3, K_3SbS_4, K_3SbS_3, K_3PO_4. After dilution with water it is acidified with HCl and filtered. In the residue may be SnS_2, Sb_2S_3 (Sb_2S_5?). These sulphides are dissolved in concentrated HCl and tested according to directions given in the analysis of the H_2S Group of Bases. In the acid filtrate may be K_3PO_4 with KCl and HCl. After evaporation to a small volume, the solution is made strongly ammoniacal and magnesia mixture added. A white crystalline precipitate of $MgNH_4PO_4$ proves the original presence of phosphorus. The precipitate may not form at once, consequently the solution should be allowed to stand for at least 30 minutes before a negative conclusion is drawn. Precipitation

is facilitated by scraping the inside of the containing vessel with a stirring rod, also by stirring.

Special Tests for Silicon, Phosphorus, Sulphur and Carbon

Silicon: A sample of the alloy is treated with 10–20 cc. of HNO_3 (1–1) in the hood. When action has ceased 20 cc. of H_2SO_4 (1–1) are added and the solution evaporated till SO_3 fumes are evolved. After cooling and carefully diluting to about 150 cc. the solution is warmed until all soluble sulphates have dissolved. The solution is filtered and the residue washed first with HCl (1–1), finally with water. The residue is then ignited in platinum and after cooling treated with HF. A platinum wire loop containing a drop of water is held in the vapors. A white cloud of silicic acid proves the presence of silicon.

Phosphorus and *Sulphur:* A separate sample is dissolved in HNO_3 (1-1) as usual and after dilution is divided into two parts to be tested for (*a*) phosphorus and (*b*) sulphur. (*a*) The portion is diluted somewhat more and warmed to about 70° C. and then 20 cc. of ammonium molybdate added followed by vigorous stirring or shaking. A yellow precipitate may be caused by arsenic or phosphorus. If arsenic is known to be absent a yellow precipitate proves the presence of phosphorus. Allow the solution to stand 30 minutes if no precipitate appears at once. The precipitate is dissolved in ammonia if arsenic is present or not known to be absent and magnesia mixture added and allowed to stand at least an hour if no precipitate appears before that time, with occasional stirring. This precipitate may be $MgNH_4PO_4$ ' or $MgNH_4AsO_4$. It is filtered off and dissolved in HCl. H_2S is passed through the hot diluted solution to test

for arsenic. If arsenic is present H_2S is passed through the solution until all the arsenic has precipitated, then it is filtered off. The filtrate should always be tried again with H_2S to ascertain if precipitation is complete. When complete the filtrate is boiled until all the H_2S has been expelled as shown by holding moist lead acetate paper in the vapors evolved. The solution is made ammoniacal, then acid with HNO_3 and heated to 70° C. Ammonium molybdate is again added as before. A yellow precipitate proves the original presence of phosphorus. (*b*) Sulphur: HCl is added to the other portion and the solution evaporated to small bulk. After dilution $BaCl_2$ solution is added. A white crystalline precipitate insoluble in hot dilute HCl proves the original presence of sulphur.

Carbon: A finely divided sample is heated in a combustion furnace in a current of oxygen and the gases caught in an excess of lime or baryta water. A white crystalline precipitate proves the presence of carbon in the original material. Consult with instructor in reference to precautions to be taken and details of operation.

CHAPTER XIV

PREPARATION OF SOLUTIONS FOR DETECTION OF THE ACIDS

For simplicity as well as to avoid side reactions the acids are obtained as the normal salts whenever possible.

Three conditions may arise:

(I) The substance is soluble in water or is in solution. (If the substance is a liquid it is cautiously poured into water and if it gives a clear solution is proceeded with as in I. If a residue is also obtained treat it as in II or III, depending upon its solubility.)

(II) The substance is insoluble or sparingly soluble in water, but readily soluble in dilute acids.

(III) The substance is insoluble in water and in dilute acids.

(I) (See I (d) if organic matter was indicated by the closed tube test.) **If the substance is soluble in water,** about a gram of the substance is dissolved in water (or a few cc. of the solution, if already in solution, are used) and its acidity or alkalinity noted. (Litmus paper test.) If not alkaline NaOH is added until the solution is alkaline and then sodium carbonate is added to make a strong solution and the solution boiled at least fifteen minutes to effect as complete decomposition as possible. The solid can be boiled with concentrated sodium carbonate solution direct. The presence or absence of NH₃ is noticed immediately after adding the NaOH and Na₂CO₃ and boiling, by means of a moist piece of red

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litmus paper held above the containing vessel. The paper should not be allowed to touch the sides of the beaker or evaporating dish. If an ammonia test is obtained, the boiling should be continued until all the ammonia has been expelled, diluting with water from time to time to prevent too great concentration of the solution. Dilute, filter the solution if necessary, and discard the residue. Neutralize the larger portion of the solution with HNO_3 until just acid, keeping the solution cool. Two cases may arise, (a) a precipitate may form with its filtrate (b), and (c) a clear solution may be obtained.

(a) The precipitate is filtered off, washed thoroughly with water and then suspended in water just decidedly acid with acetic acid. H_2S is passed through this suspension until transposition to sulphides (if any) is complete. The precipitate is filtered out and the H_2S entirely expelled from the filtrate by boiling as shown by holding a strip of lead acetate paper in the vapor. Small portions of this filtrate and (b) are added together. If no reaction occurs the larger portions of the two solutions are united; if reaction does occur the two solutions are analyzed separately.

(c) The clear solution is used for the detection of the acids. A second solution should be prepared, omitting the addition of HNO_3 for use in the analysis of the third group of acids.

(d) If organic matter is shown to be present in the closed tube test preliminary tests are made with H_2S in acid solution and in the filtrate with $(NH_4)_2S$ in ammoniacal solution to ascertain if metals of these two groups are present. If present H_2S is passed through the slightly acid solution of a gram of the unknown (or an equivalent amount of solution if not a solid) until precipitation is

complete, the precipitate is filtered off and ammonia added to filtrate till alkaline and filtered again. The last filtrate is made just acid with acetic acid and evaporated to small volume. Any precipitate of S which forms is filtered off and solid potassium carbonate added. The precipitate is filtered if necessary, the solution carefully made acid with HNO_3 followed by vigorous stirring. The precipitate ($KHC_4H_4O_6$?) is filtered out and tested for tartaric acid (see tests), and the filtrate analyzed for the remaining acids.

II. **If the substance is insoluble in water but readily soluble in acids.** (*a*) No non-volatile organic matter is present—there is no carbonization in the closed tube. .5 to 1.0 gm. is boiled direct with a little concentrated sodium carbonate and any residue filtered out. The presence or absence of NH_3 is noted by the litmus paper test immediately after adding the sodium carbonate and boiling. The filtrate should then be neutralized with HNO_3 till just acid and treated according to I *a*, I *b* or I *c*.

(*b*) The substance contains non-volatile organic matter —carbonization is observed in the closed tube. The solution from the treatment II*a* should be treated the same as under I*d*.

III. **The substance is insoluble in water and dilute acids.** Acids belonging to this classification are tested for under the analysis of the insoluble residue in the preparation of solutions for the detection of the bases unless there is indication of the presence of insoluble cyanides, especially ferrocyanides, etc., in the preliminary and subsequent treatments. (The insoluble ferro- and ferricyanides give decomposition products which are usually blue or green when boiled with HCl.) If cyanides of this character are present they are best decomposed by boiling with strong NaOH or KOH

solution in a porcelain dish. After boiling for several minutes a little Na_2CO_3 is added, the solution diluted with water and filtered. The well-washed residue is now free from cyanogen except possibly AgCN, which is tested for by suspending it in $NH_4Cl+HCl$, etc., of Group I of the Acids. The solution is tested for the acids. Divide into three parts, a small portion A and two larger portions B and C.

A—Pass H_2S through the solution a short time. This precipitates ZnS, white, PbS, black, and sulphides of the metals which might have dissolved due to presence of organic acids, etc. Mercury sulphide, however, is soluble in Na_2S, hence would not be precipitated.

A1—If no precipitate forms the solution is tested for Hg, etc., by acidifying with H_2SO_4. If a precipitate forms with H_2S in the alkaline solution it is filtered out and the filtrate tested with H_2SO_4.

B—If no precipitates were obtained with H_2S in acid or alkaline solution, then the solution is acidified with HNO_3 and the acids tested for according to the usual procedure.

C—If a precipitate forms in either case H_2S is added, one or both precipitations made as required and the sulphides removed by filtration. The solution is just acidified with HNO_3 and air drawn rapidly through to remove the excess of H_2S, and the acids tested for according to the usual procedure, remembering that H_2S reduces ferricyanic acid to ferrocyanic acid. If cobalticyanic acid is present it may be identified by adding a zinc salt to a portion of the solution. A white precipitate will be formed if such is present. (Zinc ferrocyanide and ZnS are white also.) When it is filtered off, ignited, and tested with borax bead the characteristic cobalt test should be observed.

CHAPTER XV

SYSTEMATIC ANALYSIS OF AN UNKNOWN—DETECTION OF ACIDS

In analyzing the group precipitates for their acid constituents it is best to precipitate out the first group, filter, then leave this precipitate and analyze the second group precipitate and section (A) of Group III before you examine the first precipitate for the presence of first group members, as the first precipitate is somewhat more stable than some of the more volatile acids.
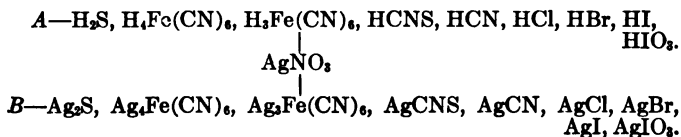
Group I

A—The precipitation of this group is always made in cold solution containing considerable dilute HNO_3 to prevent the precipitation of the members of Group II. This is accomplished by adding an equal volume of dilute HNO_3 to the prepared solution which is just acid with HNO_3 (Chapter XIV). Then a few drops of $AgNO_3$ are added and it is noticed if a permanent precipitate forms or one forms but redissolves. If none forms or it redissolves this group is absent and in the latter case some member of the next group is present with an insufficient amount of HNO_3 to keep it in solution. If a permanent precipitate forms $AgNO_3$ is added to complete precipitation. The filtrate is saved for Group II.

When the excess of HNO_3 is added to the solution certain of the strong oxidizing acids, if present, have a tendency to react with some of the reducing acids as

shown by the liberation of iodine, sulphur, or change of ferro- to ferricyanide. If such reactions occur a separate portion of the prepared solution which is just acid with HNO_3 should be taken for analysis. Then $AgNO_3$ should be added to complete precipitation, after which HNO_3 equal in volume to the resulting solution should be added.

This precipitate should not be allowed to be exposed to the light an indefinite period of time, but should always be analyzed the same laboratory period that it is obtained, as all silver salts tend to decompose to a greater or less extent. The KCN test for sulphides is always made with the freshly precipitated members of the group. In the process of analysis if no ferrocyanic, ferricyanic, hydrocyanic, or sulphocyanic acids have been detected the heating to redness preceding the halogen tests may be eliminated and the portion of the group precipitate treated directly with Zn and H_2SO_4. It should be remembered that a knowledge of the color of the silver compounds will greatly abbreviate work in this group especially. If a perfectly white precipitate is obtained from a colorless solution only the cyanide, chloride, iodate and perhaps bromide are possible. $Ag_4Fe(CN)_6$ is white, but ferrocyanide solutions are colored yellow except when such solutions are quite dilute. Ag_2S, black; $Ag_4Fe(CN)_6$, white; $Ag_3Fe(CN)_6$, brownish; AgI, yellow; and AgBr, rather light greenish yellow, are indicative of the presence of the respective acids.

A—H_2S, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, HCNS, HCN, HCl, HBr, HI,
HIO_3.
AgNO₃
|
B—Ag_2S, $Ag_4Fe(CN)_6$, $Ag_3Fe(CN)_6$, AgCNS, AgCN, AgCl, AgBr,
AgI, $AgIO_3$.

C—KCN test for sulphide.	D—NH$_4$Cl+HCl treatment. Filter.	E—Heat to redness Zn+H$_2$SO$_4$ reduction. Filter.
	Filtrate: H$_4$Fe(CN)$_6$, H$_3$Fe(CN)$_6$, HCNS, HCN. 1—FeCl$_3$ test for H$_4$Fe(CN)$_6$. 2—FeSO$_4$ test for H$_3$Fe(CN)$_6$. 3—ZnSO$_4$ precipitation of H$_4$Fe(CN)$_6$, filtration, testing of filtrate with FeCl$_3$ for HCNS. 4—CuS test for HCN. 5—K$_4$Fe(CN)$_6$ and CS$_2$ test for HIO$_3$.	Filtrate: HCl, HBr, HI. 1—Cl water and CS$_2$ test for HBr and HI. 2—KNO$_2$ liberation of I, then application of 1. 3—Precipitate AgCl, AgBr, AgI. Test for HCl by solubility in ammonia and in silver ammonia solution. 4—Special test for HI.

B—The precipitate is divided into three portions, one small (C) and two large (D) and (E).

C—To the *small portion* a solution of KCN is added in slight excess. A black residue, Ag$_2$S, proves the presence of *sulphides*. If the precipitated silver salts are allowed to remain in the light too long before this test is made a black residue of metallic silver may appear at this point.

D—*One* of the *larger portions* is treated with about 20 cc. of a *cold* mixture of equal volumes of NH$_4$Cl solution and dilute HCl. Stir vigorously. Filter and place the residue in the silver residue bottle. The filtrate is divided into four equal parts.

$D1$—Add FeCl$_3$. A deep blue precipitate " Prussian Blue " proves the presence of H$_4$Fe(CN)$_6$.

$D2$—Add a fresh solution of FeSO$_4$. A dark greenish blue precipitate, " Turnbull's Blue," proves the presence of H$_3$Fe(CN)$_6$. With small amounts of ferricyanic acid present frequently a precipitate is not discernible but the solution has the characteristic color.

D3—(If $H_4Fe(CN)_6$ is not present.)   Add $FeCl_3$ solution.   An intense red color proves the presence of HCNS.

D3—(If $H_4Fe(CN)_6$ is present.)   The solution is diluted to five or ten times the orignal amount and $ZnSO_4$ solution added in excess to precipitate the ferrocyanide. (It is best to add a few cc. of $BaCl_2$ at this point, as the precipitated $BaSO_4$ has a tendency to cause the $Zn_2Fe(CN)_6$ to settle and makes filtration easier.)   Filter and add $FeCl_3$ to the filtrate.   A deep red coloration proves the presence of HCNS.

If a negative test is obtained above for HCNS its absence is not necessarily proven, as sometimes small amounts of AgCNS may not be transposed by NH_4Cl and HCl.   Consequently if no test is obtained, treat a small portion of *E* with Zn and H_2SO_4 for several minutes, filter and test the filtrate according to *D3*.

D4—Pass H_2S through a 2 cc. portion of Copper Ammonia Solution for a minute or two.   Make the portion to be tested alkaline with NH_4OH and add it to the CuS suspension.   If the copper sulphide completely dissolves, leaving a clear solution, the presence of HCN is proven.

D5—Add $K_4Fe(CN)_6$ to a portion in a test tube and shake with CS_2.   A red to violet coloration due to free iodine proves the presence of HIO_3.

E—Transfer the *second large portion* to a porcelain crucible and heat to redness under the hood for several minutes.   Cool.   Place the crucible in a small beaker, add a few cc. of H_2SO_4 and several pieces of granulated zinc.   Allow the reduction to proceed for at least twenty minutes, warming the solution gently if necessary for reaction.   Dilute and filter.   (Place residue in silver residue bottle.)   Use filtrate for the three following tests.

E1—Add a few cc. of HNO_3 and a few drops of CS_2, then Cl water drop by drop, shaking after the addition of each drop. A violet coloration imparted to the CS_2 layer proves the presence of HI. Add more Cl water, shaking vigorously after each addition. If the violet color disappears and a yellow color is imparted to the CS_2, the presence of HBr is proven.

E2—In case a large amount of HI is present difficulty is experienced in removing the HI by oxidation with Cl water. Add a few cc. of HNO_3 and KNO_2, boil to expel the iodine. When the purple fumes cease to come off, showing that most of the iodine has been driven out of solution, add $KMnO_4$ solution to the *cooled* solution to the first appearance of a red color, then add a drop of KNO_2 solution to decolorize. Test this solution according to *E1*.

E3—(If neither HBr nor HI are present.) Add a few cc. of HNO_3 followed by a few cc. of $AgNO_3$ solution. A white curdy precipitate, AgCl, soluble in NH_4OH and reprecipitated by HNO_3, proves the presence of HCl.

E3—(If HBr only has been found to be present.) Add a few cc. of HNO_3 followed by $AgNO_3$ solution, filter and discard filtrate. Digest the precipitate with Silver Ammonia Solution, filter and add HNO_3 to the filtrate. A white curdy precipitate, AgCl, soluble in NH_4OH and reprecipitated by HNO_3 proves the presence of HCl.

E3—(If HI or HI and HBr are present.) Add a few cc. of HNO_3 followed by $AgNO_3$ solution, filter and treat the precipitate with cold NH_4OH. AgCl and some of the AgBr are dissolved. Filter, add HNO_3 to the filtrate to reprecipitate the AgCl and AgBr. Treat this precipitate with Silver Ammonia Solution according to directions " if HBr is present," *E3*.

E3—(If HI or HI and HBr are present.) Alternate procedure. Add NaOH until just alkaline, then add 5 cc. of acetic acid, dilute to about 50 cc. Add about .5 gm. of potassium persulphate and heat until all the iodine has been expelled, adding more persulphate if necessary. Add 10 cc. of sulphuric acid, heat to boiling to liberate the bromine, adding more persulphate if required. Boil until the bromine is entirely expelled. Water should be added from time to time to replace that lost by evaporation, maintaining the original volume. After cooling and diluting somewhat a few drops of silver nitrate solution are added. A white, curdy precipitate soluble in NH_4OH and reprecipitated by HNO_3 proves the presence of HCl. After adding the acetic acid and persulphate one can take a small portion of the solution and shake it with CS_2 for the iodine test if the iod ne vapors are not pronounced and also test for bromine following the expulsion of the iodine by shaking CS_2 with a small portion of the solution after the addition of sulphuric acid.

E4—In case an iodate has been found, a special test is made for iodide by acidifying a small portion of the sodium carbonate solution in a test tube with dilute H_2SO_4 and shaking the solution with CS_2. A violet coloration proves the presence of iodides.

GROUP II

A—A piece of litmus paper is slipped down the side of the beaker containing the filtrate from Group I and NH_4OH added gradually with constant stirring of the solution till *one drop* will make the solution alkaline, keeping the solution cool. A large excess of NH_4OH is to be avoided. Make just acid with HNO_3. Only one or two drops of HNO_3 should be necessary to make the solution acid,

5 cc. of $NaC_2H_3O_2$ solution are added, followed by slow addition of silver nitrate until precipitation is complete. (It must be remembered that some silver nitrate is present in solution before neutralization due to the slight excess added to precipitate the first group. Precipitation may occur dur'ng the process of neutralization due to the presence of $AgNO_3$.) Filter. To the filtrate add 2 cc. of $NaC_2H_3O_2$ and a drop or two of $AgNO_3$ to ascertain if precipitation is comp ete. If not complete add sufficient $AgNO_3$ to make it complete. Should another precipitate form it should be added to the original. The filtrate is saved for Group III.

In the precipitation of this group a large excess of $AgNO_3$ may give insoluble $AgC_2H_3O_2$, white, crystalline. If it seems to appear the addition of water will effect its solution. However, its presence in the precipitate does not interfere with any tests of this group.

$H_2CrO_4, H_3AsO_4, H_3AsO_3, H_3PO_4, H_2C_2O_4, H_2SO_3.$

$AgNO_3$
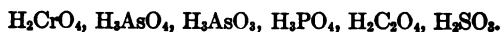
$Ag_2CrO_4, Ag_3AsO_4, Ag_3AsO_3, Ag_3PO_4, Ag_2C_2O_4, Ag_2SO_3.$ Filter. Save filtrate.

Treat Precipitate with HCl.   Filter.

Filtrate may contain either B—$H_2CrO_4, H_3AsO_4, H_3PO_4, H_2C_2O_4$ in a yellow solution, or C—H_3AsO_3, H_2SO_3 or $H_3AsO_4, H_3PO_4, H_2C_2O_4$ in a colorless solution.

B—Add Na_2SO_3.   Boil off SO_2.   Yellow color of chromate changes to green.

$B1$—Pass in H_2S. Filter.		$B3$—Remove chromium by boiling with Na_2CO_3 and filtering. Make $CaCl_2$ test for $H_2C_2O_4$ in acetic acid solution.
Precipitate: As_2S_3, yellow, soluble in Na_2CO_3, reprec. by acids, proves H_3AsO_4.	$B2$—Filtrate: Boil off H_2S. Make $(NH_4)_2MoO_4$ test for H_3PO_4 in HNO_3 solution.	

C—Not colored yellow due to the absence of chromates. Divide into 5 portions.

C1—Add Cl water. Make $BaCl_2$ test for the oxidized H_2SO_3.
C2—Make Ag_3AsO_4 color test for H_3AsO_4.
C3—Use Al+KOH test for H_3AsO_3.
C4—Remove arsenic with H_2S. Make $(NH_4)_2MoO_4$ test for H_3PO_4 in the filtrate.
C5—Test for $H_2C_2O_4$ in acetic acid solution by adding $CaCl_2$.

The precipitate is digested with HCl with vigorous stirring and then filtered. The residue should be placed in the silver residue bottle. The filtrate is tested for the members of this group. Dilute HCl in all cases must be used for the transposition of the silver salts, as concentrated HCl dissolves an appreciable quantity of AgCl and when the solution is diluted, as in the test for sulphites by the addition of Cl water, AgCl may precipitate. This is entirely avoided by the use of the dilute acid and the transposition is fully as effective.

B—The sulphite and arsenite are oxi ized to sulphate and arsenate in hot alkaline, cold neutral or cold acid solutions and much more rapidly if the last two are hot, by an excess of chromate, hence the divisions *B* and *C*.

Add a few very small crystals of Na_2SO_3, heat till the SO_2 fumes are comp etely expelled. (Odor will disappea .) The yellow or reddish-yellow color of the solution changes to green, proving the presence of H_2CrO_4. If this acid is present in small amounts the green will not be discernible and the solution appears colorless. Divide the solution into two parts.

B1—Dilute *one portion* with an equal volume of water, heat to boiling, pass in H_2S to complete precipitation. Filter. Use filtrate for *B2*. If H_3AsO_4 was originally present it precipitates as As_2S_3, yellow, as the

Na_2SO_3 treatment reduces the arsenic to arsenous acid. The precipitate should dissolve in 5% Na_2CO_3, warming if necessary, and reprecipitate on the addition of HCl.

B2—Boil off the H_2S from the filtrate, add NH_4OH till just alkaline. Without filtration add an excess of HNO_3. Warm to about 70° (this is about the temperature at which one can comfortably keep the hand on the vessel containing the solution), add an equal volume of $(NH_4)_2MoO_4$ and warm again. A yellow precipitate proves the presence of H_3PO_4. The formation of a white precipitate is due to heating the ammonium molybdate too highly, causing decomposition. It is absolutely necessary to have all the arsenic precipitated and the H_2S boiled from the filtrate before this test is applied.

B3—Add Na_2CO_3 till the *second portion* is alkaline, followed by 5–10 cc. in excess, boil, filter. To the filtrate add acetic acid in decided excess. Add $CaCl_2$ solution and warm. Allow to stand twenty or thirty minutes if no precipitate forms at first. A white crystalline precipitate proves the presence of $H_2C_2O_4$.

C—In the absence of H_2CrO_4 the solution is colorless. H_3AsO_4 and H_2SO_3 can not both be present, as the sulphurous acid will reduce the arsenic to arsenous acid, hence if sulphurous acid is found arsenic acid need not be tested for. H_3AsO_3, H_3PO_4, and $H_2C_2O_4$ may be present with one of the two just mentioned; however, with an excess of $H_2C_2O_4$ the H_3AsO_4 may be reduced. Divide the solution into five portions.

C1—Add Cl water, heat to boiling and add $BaCl_2$ solution. Allow to stand at least twenty minutes if no precipitate forms immediately. A white crystalline precipitate, insoluble in HCl, proves the presence originally of H_2SO_3.

$C2$—(Performed only in the absence of H_2SO_3.) Add NH_4OH till just alkaline, then make just acid with acetic. Add a few drops of $AgNO_3$. A chocolate-brown precipitate proves the presence of an arsenate.

$C3$—To the solution in a test tube add aluminum turnings and KOH. Insert a piece of cotton to dry the arsine. Fit over the mouth of the tube a piece of filter paper upon which a small crystal of $AgNO_3$ is placed. Warm the solution. If H_3AsO_3 is present the crystal turns yellow and then black. (Do not inhale the gas—it is poisonous.)

$C4$—If arsenous or arsenic acid is present, dilute, heat to boiling, pass H_2S through the solution to complete precipitation of the arsenic. If considerable arsenic acid is present add a few *small* crystals of Na_2SO_3 and boil until odor of SO_2 has completely disappeared before passing the H_2S. The solution should be decidedly acid with HCl. Boil H_2S completely from the filtrate and test according to $B2$.

$C4$—If sulphurous acid is present boil until the odor of SO_2 is completely gone, make alkaline with NH_4OH and test according to $B2$.

$C5$—Make the solution ammoniacal then add acetic acid in decided excess, heat to boiling, add $CaCl_2$ solution and heat again. Let stand at least thirty minutes if no precipitate forms at once. A white finely divided crystalline precipitate proves the presence of $H_2C_2O_4$.

$Ag_2C_4H_4O_6$ and $AgBO_2$, both white, may precipitate in this group, but they do not interfere with any tests of this group. They are best tested for in Group III. Their presence will have been indicated in the preliminary tests.

GROUP III

This group is divided into three divisions to be tested for in A and B—the filtrate from group two, C—the Na_2CO_3 solution, and D—the original solid or solution.

A—Filtrate from Group II. Divide into two portions, one large and one small. A—Small portion: $H_2SO_4 +$ Zn reduction. Filter. Test filtrate with $AgNO_3$. AgCl proves $HClO_3$. AgBr proves $HBrO_3$. See E, Group I. B—Large portion: Silver is removed by NaOH. Add $BaCl_2$ to HCl solution.	C—Na_2CO_3 solution. Removal of permanganates, manganates, and chromates by SO_2 reduction in HCl solution. Precipitation of Cu if present by H_2S. Na_2CO_3 precipitation of chromium and manganese. Use filtrate.	D—Original Solution or Solid. D1— $Ca(OH)_2$ test for H_2CO_3 D2—Ag_2S test for H_2S. D3— SiO_2 test for silicates. D4— Etching test for HF.

$BaSO_4$ proves H_2SO_4.	B1—Add Br water and $BaCl_2$ to filtrate.			
	$BaSO_4$. proves H_2SO_3.	B2—Make filtrate ammoniacal, then acid with acetic. $CaCl_2$ test for $H_2C_2O_4$.		

B3—Special test for H_2SO_3 and H_3AsO_3, which is sometimes necessary.

	C1—Copper test for $H_2C_4H_4O_6$. C2—Cobalt sulphide and odor tests for $HC_2H_3O_2$. C3—Flame test for H_3BO_3. C4—$FeSO_4$ test for HNO_2 and HNO_3.

A—The *small portion*—Add a few pieces of granulated zinc and a few cc. of H_2SO_4, boil several minutes, filter. Add a few cc. of $AgNO_3$ solution to the filtrate. A white curdy precipitate, soluble in NH_4OH and reprecipitated by HNO_3 proves the presence originally of $HClO_3$. If the precipitate is not perfectly white and easily soluble in NH_4OH and silver ammonia solution it may contain AgBr, in which case test for HCl and HBr accord-

ing to procedure E, Group I. If HBr is found in the reduced solution this proves the original presence of $HBrO_3$.

B—The *large portion*. Add NaOH till alkaline, filter. Make the filtrate decidedly acid with HCl and filter if necessary. Add $BaCl_2$ solution. A white precipitate insoluble in HCl proves the presence of H_2SO_4. Add $BaCl_2$ to complete precipitation. Let stand a few minutes. Filter through a double filter, the under one being a hardened filter paper. This prevents the $BaSO_4$ from running through the paper better than a single paper. Use filtrate for $B1$.

$B1$—To the filtrate add a few more cc. of $BaCl_2$ solution to insure complete removal of the sulphate. Add Br water until the solution is colored very slightly yellow. The H_2SO_3 not precipitated in the second group is oxidized to sulphate and precipitates at this point. A white crystalline precipitate insoluble in HCl proves the presence of H_2SO_3. Add sufficient $BaCl_2$ to give complete precipitation. Filter. Use filtrate for $B2$.

$B2$—To the clear filtrate add a few cc. of $CaCl_2$ solution, make just ammoniacal then acid with acetic. Heat to boiling. Allow to stand at least thirty minutes if no precipitate forms immediately. A white finely divided precipitate proves the presence of $H_2C_2O_4$.

Ag_2SO_3 and $Ag_2C_2O_4$, especially the former, have an appreciable solubility in water, sufficient to cause small amounts of the two acids to be missed in some cases. Hence they are tested for in the filtrate from the second group as well as in the group proper.

$B3$—If a H_2SO_4 test is obtained and no H_2SO_3 or H_3AsO_4 test obtained and no H_3AsO_3, add HCl to a portion of the Na_2CO_3 solution C till just acid, stir vigorously to remove the CO_2 and neutralize with NH_4OH, leaving the solution just alkaline. Add $BaCl_2$ to com-

plete precipitation, filter one-half of the solution and test the filtrate for H_3AsO_3 according to $C3$, Group II. To the precipitate and the remainder of the solution add HCl in excess, filter. Add a few more cc. of $BaCl_2$ to insure complete removal of the H_2SO_4. To the filtrate add Br water and warm. A white crystalline precipitate of $BaSO_4$, insoluble in HCl, proves the presence of H_2SO_3, which had been oxidized before the previous tests were applied.

C—A portion of the prepared Na_2CO_3 solution is used for the following tests. Note the color of the solution. If pink to purple permanganates are present. Manganates would tinge the solution green. Chromates color the solution yellow. Should any of these be present add H_2SO_4 till acid, then about 10 cc. in excess. Add a crystal or two of Na_2SO_3, then boil off the SO_2. (If copper and a tartrate are both present in the original the solution will be colored deep blue. In such cases the copper should be removed by H_2S from dilute H_2SO_4 solution.) Add Na_2CO_3 in excess and boil again. Filter and use the filtrate for the following tests:

$C1$—See page 99 for the copper tartrate and potassium acid tartrate test for $H_2C_4H_4O_6$.

$C2$—See page 97 for the cobalt sulphide test for $HC_2H_3O_2$, also identify by odor tests, if HCN, etc. are absent.

$C3$—See page 98 for the flame test for H_3BO_3.

$C4$—See pages 99–101 for the ferrous sulphate test for HNO_2 and HNO_3. If HNO_2 is present the portion to be tested for HNO_3 must be warmed with $HC_2H_3O_2$ until all the HNO_2 is expelled before applying the test for HNO_3.

If arsenous, sulphurous, ferrocyanic or hydriodic acids have been found the test for nitrous acid can be dis-

pensed with, as none of these could exist in the presence of nitrous acid, being oxidized by it.

D—Use the original solution or solid. If a solution is being analyzed the following conclusions may be drawn: 1st—The sulphide, if present, was found in the first group; 2nd—Fusion is not necessary to put the silicate in solution; 3rd—If a silicate is present the acetic acid precipitation preceding the HF test can be made direct; 4th—If no silicate is present the fluoride precipitation with $CaCl_2$ can be made direct by making the solution alkaline (if not already so) then acid with acetic, and the HF test applied as usual. (Acid solutions containing HF must not be kept in glass vessels.)

D1—See page 101 for the $Ca(OH)_2$ test for H_2CO_3.

D2—See page 87 for the sulphide fusion test for H_2S.

D3—See page 103 for the silicate test.

D4—See page 103 for the etching test for HF.

Alternate Scheme for the Identification of the Acids.

In this scheme the acids are divided into groups according to behavior toward group reagents.

1. The Silver Group.   Those acids which form silver salts insoluble in dilute nitric acid: H_2S, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, HCN, HCNS, HIO_3, HCl, HBr, HI. $AgNO_3$ is the group reagent.

2. The Barium Group.   Those acids which form barium salts insoluble in neutral or alkaline solution: H_2SO_4, H_2SO_3, H_3AsO_4, H_3AsO_3, H_3PO_4, H_3BO_3, H_2CO_3, H_2CrO_4, HF, $H_2C_2O_4$, $H_2C_4H_4O_6$, H_2SiO_3, HIO_3. Barium chloride is the group reagent, although calcium chloride is also added, inasmuch as certain of the acids, particularly oxalic and hydrofluoric acids, form more insoluble salts with calcium than with barium.

3. The Soluble Group.   Those acids which have salts which are too soluble to have a group reagent: HNO_3, HNO_2, $HClO_3$, $HBrO_3$, $HC_2H_3O_2$.

The solutions are made up as in the previous scheme except that the Na_2CO_3 solution is not acidified with HNO_3.

1. The Silver Group. A small portion of the sodium carbonate solution is acidified with HNO_3 and $AgNO_3$ added. If no precipitate forms the acids of this group are absent. If a precipitate forms one or more members of this group are present (knowledge of the colors of the various silver salts is a good aid at this point), and must be tested for in separate portions of the sodium carbonate solution made acid or alkaline to suit the particular reaction. See pages 80 to 88.

Identify H_2S by the lead acetate reaction.

Identify $H_4Fe(CN)_6$ by the $FeCl_3$ reaction.

Identify $H_3Fe(CN)_6$ by the $FeSO_4$ reaction.

Identify HCN by the CuS reaction.

Identify HCNS by the $FeCl_3$ reaction, removing the $H_4Fe(CN)_6$ if present with $ZnSO_4$ in HCl solution, filtering off the $Zn_2Fe(CN)_6$, and testing filtrate.

Identify HIO_3 by liberation of iodine with KI, by ignition to iodide and testing for the latter, also by precipitation of $Ba(IO_3)_2$.

Identify HI, HBr, HCl by the persulphate reaction or the use of the varied solubility of silver salts in ammonia and silver ammonia solution.   (It is best to precipitate Group I as silver salts, filter, ignite the silver salts, treat with $Zn+H_2SO_4$, filter, then test filtrate as above noted.)

2. The Barium Group.   A small portion of the sodium carbonate group is made just acid with HCl, then NH_4OH added till slightly alkaline. A few drops of $BaCl_2$ and $CaCl_2$ are then added and observation taken. If no

precipitate forms the members of this group are absent. If a precipitate forms one or more members of this group are present and must be tested for in separate portions of the sodium carbonate solution made acid or alkaline, etc., to suit the particular reaction. See pages 89 to 105 for tests for members of this group.

Identify H_2SO_4 by the insolubility of $BaSO_4$ in acids.

Identify H_2SO_3 by oxidation, then the test for H_2SO_4. (H_2SO_4 must be first removed by precipitation with $BaCl_2$.)

Identify H_3AsO_4 by color of silver salt, by liberation of iodine with KI and by precipitation with H_2S and magnesia mixture.

Identify H_3AsO_3 by the Al+KOH test.

Identify H_3PO_4 by the molybdate test in absence of arsenous and arsenic acids. If these acids are present remove them by H_2S in HCl solution, boil off H_2S and perform molybdate test in nitric acid solution.

Identify H_3BO_3 by flame test (alcohol+H_2SO_4).

Identify H_2CO_3 by evolution of CO_2, then turbidity of lime-water.

Identify H_2CrO_4 by $BaCrO_4$ precipitation, and by KI reaction liberating iodine and forming a green solution.

Identify HF by etching of glass.

Identify $H_2C_2O_4$ by precipitation of CaC_2O_4 in acetic acid solution.

Identify $H_2C_4H_4O_6$ by $CuC_4H_4O_6$ or $KHC_4H_4O_6$ reaction and charring with H_2SO_4.

Identify H_2SiO_3 by HF reaction.

HIO_3 is tested for in Group I.

3. The Soluble Group. Separate portions of the sodium carbonate solution are made acid or alkaline, etc. to suit the particular reaction and used for the following tests.

See pages 95 to 105 for test reactions of members of this Group.

Identify HNO_2 by brown ring test and KI reaction.

Identify HNO_3 by brown ring test after removing HNO_2.

Identify $HClO_3$ and $HBrO_3$ by removal of Group I with excess of $AgNO_3$ in HNO_3 solution, and removal of $AgNO_3$ from filtrate by addition of NaOH till alkaline. Filter. Evaporate filtrate to dryness and ignite. Dissolve in water and test for bromide and chloride according to Group I.

Identify $HC_2H_3O_2$ by cobalt sulphide and odor tests.

EXERCISE

(These questions apply essentially to the first scheme given for the identification of the acids.)

1. Why is it essential to have an excess of dilute nitric acid present when the first group of acids is precipitated? Will a large excess of strong acid affect the precipitation? How?

2. What acids of the first group will be precipitated in the second group if incomplete precipitation occurs in the first case?

3. What acids of group one will interfere if precipitated in group two?   How?

4. Under what conditions is it necessary to test for a sulphide in acid group three?

5. How many acids will oxidize hydrogen sulphide?

6. (a) The presence of what acids eliminates the presence of nitrous acid?   Why?   (b) The presence of nitrous acid eliminates what acids?   Why?

7. What acids will interfere with the " brown ring " test for nitric acid?   How?   How can they be removed?

8. Will any foreign reactions be introduced in the third group of acids if the acids of groups one and two are not precipitated preceding this group?   Explain.

9. What acids can be tested for directly in the original sodium carbonate solution without any interferences from the others which may be present?

10. Why can acid group one not be precipitated from a hot solution?

11. Why can not acetic, boric, tartaric, nitric and nitrous acids be tested for in the filtrate from acid group two?

12. Why is it possible to make the two main divisions of the second acid group?

CHAPTER XVI

SYSTEMATIC ANALYSIS OF AN UNKNOWN

Detection of the Bases

A—The prepared solution or solutions from Chapter XIII are used for the systematic analysis.

Group I

To the acid solution add a few drops of HCl to test for the presence of the members of this group. If a precipitate forms it may be AgCl, HgCl, $PbCl_2$, BiOCl, or SbOCl. Add HCl to complete precipitation. Filter. To a portion of the precipitate or the original solution add HCl in excess and warm. If the precipitate entirely redissolves, without reprecipitating on cooling, it is probably bismuth or antimony. If the precipitate entirely dissolves with a moderate excess of the dilute acid in the above test, treat the entire precipitate with an excess of HCl and proceed as though no precipitate had been obtained with the precipitation of the second group. If the precipitate does not completely redissolve, filter and add to filtrate considerable water to test for the presence of antimony or bismuth. Should a test be obtained, treat the whole group precipitate with sufficient HCl to redissolve the antimony and bismuth but avoid a large excess of HCl, warm, filter, and add this filtrate to the original filtrate. Save the combined filtrates for Group II.

Wash the precipitate or residue twice and analyze according to B.

A—*Solution may contain lead, silver and mercurous mercury.*

HCl

$PbCl_2$, $AgCl$, $HgCl$.
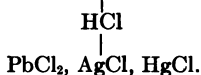
B—Treat with hot water.

B—Residue: $HgCl$, $AgCl$, white. Add NH_4OH.		D—Solution: $PbCl_2$. Use K_2CrO_4 and KI tests for lead.
Residue: $Hg+HgNH_2Cl$, black, proves mercury.	C—Solution. $2AgCl.3NH_3$. HNO_3 reprecipitates $AgCl$, white, curdy.	

B—Treat the group precipitate with hot water. Filter while hot. The $PbCl_2$ dissolves and lead is tested for according to D. The chlorides of silver and mercury remain. Pour about 5 cc. of strong NH_4OH repeatedly through the filter containing the residue. If a black residue, Hg and $HgNH_2Cl$, is obtained, the presence of *mercurous mercury* is proved.

C—The filtrate contains $2AgCl.3NH_3$. Acidify with $\underline{HNO_3}$. If $AgCl$, white, curdy, precipitates the presence of *silver* is proved.

D—Divide the hot water extraction into two parts and test as follows:

1—Add KI solution. PbI_2, yellow, precipitates; soluble in hot water, crystallizing in thin shining plates on cooling, proving the presence of *lead*.

2—Add K_2CrO_4 solution. $PbCrO_4$, yellow, precipitates; soluble in $NaOH$, proving the presence of *lead*.

(If the $PbCl_2$ solution is sufficiently concentrated, frequently long needle-like crystals of the chloride deposit on cooling.)

Group II

A—To the combined filtrates from the preceding group · add HCl if necessary until the proportion of dilute acid to water is about one to ten. (If HNO_3 has been used to effect solution, it is boiled off, adding HCl to replace the HNO_3. Two evaporations to small bulk (not to dryness) usually removes a sufficient quantity of the HNO_3 to prevent the precipitation of sulphur caused by oxidation of the H_2S. The solution is then made up to the proper concentration with HCl and water.) Heat to boiling, pass a slow current of H_2S until the solution is cold. Filter. Add an equal volume of water. Heat to boiling, pass a slow current of H_2S to test for the complete precipitation of the members of this group. Wash the precipitate two or three times with hot water containing a little H_2S. Save the filtrate for Group III.

NOTE: The presence of HCl is necessary to insure complete precipitation of the arsenic, antimony and tin, as the sulphides of these elements are not completely precipitated from neutral solutions or from solutions which contain these elements in the form of acids because of the formation of soluble compounds or colloidal solutions of the sulphides. HCl prevents the formation of such solutions and causes the sulphides to be precipitated in a compact form, making filtration easy. HCl also prevents the precipitation of the members of the next group, which are precipitated from alkaline, neutral, or in the case of zinc especially, from very slightly acid solutions by H_2S. As_2S_5 precipitates very slowly from solutions of arsenic acid and completely only after several hours. By heating the solution before the treatment with H_2S the reduction of arsenic to arsenous

acid takes place more rapidly and from the latter condition As_2S_3 precipitates readily. If arsenic acid is known to be present it may be reduced by the addition of Na_2SO_3 and boiling off the excess of SO_2. The excess of SO_2 must be boiled off completely, otherwise sulphur will be precipitated when H_2S is passed through the solution. This treatment may also precipitate lead and members of Group IV as sulphates. Chromates, permanganates and manganates, coloring the solution red or yellow, purple and green respectively are reduced by Na_2SO_3 likewise. The passage of H_2S may reduce these solutions completely without the addition of Na_2SO_3, the reduction being greatly facilitated by the presence of considerable HCl.

B—A small portion of the group precipitate is treated with yellow ammonium sulphide and warmed. If the under dawd: precipitate completely dissolves procedure C can be dispensed with, as only members of H are present. If complete solution is not effected members of C are present and those of H may or may not be present. Filter the ammonium sulphide solution and make acid with HCl. If no flocculent or colored precipitate is formed members of H are absent.

(If on the addition of dilute HCl to the ammonium polysulphide solution a pure white precipitate forms arsenic, antimony and tin are absent. If a small and dark colored or unpronounced yellow or orange precipitate mixed with sulphur results; thus causing one to doubt the presence of sub-group H, one can apply this simple test: Heat with 15–20 cc. of strong NH_4OH almost to boiling for about 5 minutes, filter, test residue for copper if it has not already been found, add a few drops of $(NH_4)_2S$ to filtrate. Filter, heat filtrate to boiling, make acid with HCl, shake, treat precipitate as usual.

The S and CuS are not dissolved by NH_4OH. Any small quantity of HgS will be precipitated by $(NH_4)_2S$, so that the final HCl precipitate can contain only members of this group and a little sulphur.

OUTLINE OF GROUP ANALYSIS

A—The solution may contain mercury, lead, bismuth, copper, cadmium, arsenic, antimony and tin.

$$H_2S$$

A—HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5, Sb_2S_3, SnS, SnS_2 ($BaSO_4$).

B—Treat with $(NH_4)_2S_x$. Filter.

C—Residue: HgS, ($BaSO_4$), PbS,Bi_2S_3, CuS, CdS. Treat with hot HNO_3. Filter.					*H*—Filtrate: Sulpho salts of As, Sb, Sn. Add HCl. Filter.		
HgS, ($BaSO_4$) black. SnCl₂ test for mercury.	*D*—Filtrate: Nitrates of Cu, Pb, Bi, Cd. Add H_2SO_4. Boil to SO_3 fumes. Dilute, filter.				Boil sulphides with conc. HCl, add equal volume of water. Filter.		
	PbSO₄ K₂CrO₄ test for lead.	*E*—Filtrate: Sulphates of Cu, Bi and Cd. Add NH_4OH. A blue solution proves the presence of copper. Filter.			As_2S_3, yellow $(NH_4)_2CO_3$ solubility test proves arsenic	*I*—Filtrate: Fe reduction. Filter.	
			Bi(OH)₃ Oxychloride or stannite test for bismuth.	*F*—Filtrate: Cu andCd ammonio sulphates. *G*—Make acid with HCl. Pass in H_2S.		Sb, black. Sulphide test for antimony.	*J*—Filtrate: SnCl₂,SbCl₃. H_2S precipitation. Treat sulphides with 5% Na_2CO_3.
				CuS, black. CdS, yellow. If black, dissolve CdS in H_2SO_4. Filter. Dilute, add H_2S. Yellow CdS proves cadmium.		SnS, Alkali solubility test.	*K*—Filtrate: Add HCl-Sb_2S_3, orange.

Occasionally some CuS or HgS dissolves in $(NH_4)_2S_x$, giving a reddish brown or black precipitate when the resulting solution is acidified with HCl. This, however,

very seldom affects results except when the quantity of copper or mercury present is very small, in which cases the corresponding precipitates obtained above should be tested for these elements.)

If a precipitate of this nature appears, treat the entire group precipitate with the yellow ammonium sulphide—10 cc. are usually sufficient. Warm, but do not boil. Stir occasionally and filter after about three minutes' digestion. Wash first with yellow ammonium sulphide and then with water. Test the precipitate according to C and the filtrate according to H.

C—Digest the residue with hot dilute HNO₃. Filter, wash the residue, if any, with hot dilute HNO₃ at first, then with hot water. Test filtrate according to D. A black residue indicates the presence of mercury. Dissolve in aqua regia, expel excess of acid by evaporating to small bulk. Dilute with water and add SnCl₂ solution. If *mercury* is present HgCl, white, metallic mercury, black, or a gray mixture of these two is precipitated, depending upon how much of the reagent is added. HgCl gives a black residue when treated with NH₄OH. Should a white residue remain after dissolving the HgS in aqua regia it may contain some member of the fourth group.

Occasionally if a strong oxidizing agent is present the H₂S or SO₂ treatment will form considerable H₂SO₄, which will react with barium, strontium or calcium and lead, precipitating the sulphates. Only in extreme instances will lead, calcium or strontium be completely precipitated thus, and the tests for these elements are not greatly interfered with. However, if a white residue remains, after treating the residue from the HNO₃ extraction in the mercury with aqua regia, indicating something beside mercury, it should be fused

with Na_2CO_3, the fusion extracted with water, filtered, the residue dissolved in dilute HCl, NH_4OH and $(NH_4)_2CO_3$ added, and tested for the presence of members of Group IV or added directly to the filtrate from Group III.

D—A few cc. of H_2SO_4 are added to the nitrate solution and evaporation carried on till the dense white fumes of SO_3 are evolved copiously. (This should be done under the hood where the draft is good.) Cool, dilute cautiously, pouring the sulphuric acid into water, not water into the acid. Filter. Wash the precipitate with water containing a little H_2SO_4. See *E* for filtrate treatment. A white crystalline precipitate indicates the presence of lead. Dissolve in a hot solution of ammonium acetate containing a little free acetic acid. Add a solution of K_2CrO_4. The appearance of a yellow precipitate, $PbCrO_4$, soluble in considerable NaOH, proves the presence of *lead*.

E—To the sulphate solution add NH_4OH to distinct alkaline reaction. Filter and wash the precipitate with hot water. The filtrate is treated according to *F*. A white precipitate, $Bi(OH)_3$, indicates the presence of *bismuth*. Confirm by adding HCl to the precipitate on the filter paper, allowing the solution to drop into water; a white precipitate, BiOCl, proves the presence of this element. The $Bi(OH)_3$ can be treated with a fresh solution of alkali stannite, which gives black metallic bismuth. The alkali stannite is made by adding a solution of NaOH or KOH to a solution of $SnCl_2$ until the precipitate which forms at first just redissolves.

F—A blue solution containing $CuSO_4 \cdot 4NH_3$ proves the presence of *copper*.

G—HCl is added to the ▮▮▮▮ution containing the copper and cadmium ammonia ▮▮▮▮ill acid followed by a slight

excess of the same reagent. Pass in H_2S to complete precipitation. Filter and reject filtrate. A yellow precipitate proves the presence of *cadmium*, provided it is insoluble in yellow ammonium sulphide. If copper is present, filter off the precipitate and boil immediately with *avoid too much acid* dilute H_2SO_4. Filter. Reject the residue. Dilute and pass H_2S through the filtrate. A yellow precipitate proves the presence of *cadmium*.

G (optional)—If the addition of ammonia did not produce a blue color then acidify with HCl and pass H_2S into the solution. A yellow precipitate insoluble in yellow ammonium sulphide proves the presence of cadmium. If the ammoniacal solution is blue, due to the presence of copper, potassium cyanide solution is added until the blue color disappears, then H_2S is passed into the solution. A yellow precipitate proves the presence of *cadmium*.

H—The filtrate from procedure *B* contains the sulpho salts of arsenic, antimony and tin. Add HCl until the solution is acid to litmus. Filter. Reject the filtrate. *under good* Boil the sulphides with concentrated HCl, add an equal *omit* volume of water and pass H_2S through the solution for a few minutes. Filter. See procedure *I* for treatment of filtrate. A yellow residue, As_2S_5, soluble in boiling $(NH_4)_2CO_3$ solution and reprecipitating when acidified with HCl, proves the presence of *arsenic*. If the arsenic is present in small amounts H_2S should be passed through the solution after acidifying in the final test to insure complete precipitation.

I—This solution containing the chlorides of antimony and tin should not have a volume of over 20-30 cc. and should be contained in a small beaker. Add a small coil of iron wire or a few iron nails. (The iron must be free from the elements of this group, naturally.) Warm under the hood till the antimony is precipitated,

adding water if necessary to keep the volume constant. Usually 10–15 minutes will suffice. Cool, dilute and filter. See *J* for the filtrate. Metallic antimony, black, precipitates. Dissolve in a small quantity of concentrated HCl adding a few crystals of KClO₃ as needed to effect solution. Boil off the chlorine, adding more HCl if necessary to decompose the chlorate. Dilute and pass H_2S through the hot solution. An orange colored precipitate, Sb_2S_3, proves the presence of *antimony*.

J—Having the concentration of HCl about 1-10, pass H_2S through the warm solution to complete precipitation, add an equal volume of water, filter. Discard the fi trate. Boil the sulphides with 5% Na_2CO_3 solution, adding water to keep the concentration of the solution uniform if the boiling is continued more than a few seconds. Filter. The filtrate is tested by *K*. Boil the residue a moment with NaOH solution which is at least of 10% strength to remove any iron which may come down with the sulphides. Filter if necessary and discard the residue. Make the filtrate or solution acid with HCl, add H_2S if necessary. A brown to black precipitate, SnS, proves the presence of *tin*.

K—Add HCl to the solution till acid, adding H_2S if necessary. An orange precipitate, Sb_2S_3, proves the presence of *antimony*. This test may be omitted if antimony has been found by procedure I.

GROUP III

A—The procedure for the analysis of this group is dependent upon the acids present. Fluorides, borates, oxalates, tartrates and phosphates interfere and must be removed during the process of analysis. The oxalates and tartrates have already been removed.

If fluorides are present, the filtrate from the second

group is treated with a slight excess of H_2SO_4 (10–15 cc.) and the solution evaporated almost to dryness in a porcelain evaporator (platinum is preferable), thus volatilizing the HF and most of the H_2SO_4. This operation is performed under the hood where the draft is good. Cautiously dilute with water, stir for a few seconds to effect solution of the members of this group. (A residue at this point consists of alkaline earth sulphates. Filter, fuse the residue with Na_2CO_3 in a platinum crucible, extract the cold fused mass with water, filter, dissolve the residue in HCl and add the solution to the $(NH_4)_2S$ filtrate.)

If borates are present, the boric acid is volatilized as ethyl borate by evaporating two or three times practically to dryness with equal parts of concentrated HCl and alcohol. When all the boric acid is expelled, as ascertained by the flame test, the residual alcohol and acid are boiled off and the solution diluted with water preceding the addition of $(NH_4)_2S$. .

The filtrate from group two, free from fluorides, borates, oxalates and tartrates, is treated with 20 cc. of NH_4Cl and made just alkaline with NH_4OH. $(NH_4)_2S$ (colorless ammonium sulphide) is added to complete precipitation, although in very slight excess. A large excess of $(NH_4)_2S$ is to be avoided, hence 10 cc. of $(NH_4)_2S$ is added slowly with constant stirring of solution. The solution is warmed and stirred to coagulate precipitate, and a few cc. more of $(NH_4)_2S$ added if precipitation is incomplete. Filter. Wash with H_2S water. If the filtrate is dark, it may contain some nickel. Boil it. This decomposes the excess of $(NH_4)_2S$ and evaporates the excess of NH_4OH, allowing the NiS to precipitate. In special cases some chromium, as $CrCl_3 \cdot 4NH_3$ or aluminum as $Al(ONH_4)_3$ has a slight

tendency to remain in solution. Boiling also causes the precipitation of their hydroxides. This precipitate, if any, is added to the original group precipitate.

NOTE: In this group are precipitated the hydroxides of aluminum, titanium and chromium and the sulphides of the other members. Magnesium will likewise precipitate if the quantity of NH_4Cl present is insufficient to form $MgCl_2 \cdot 2NH_4Cl$ with all the magnesium present. The presence of NH_4Cl also prevents the formation of pseudo-solutions, causes a more compact form of the sulphides and prevents the precipitation of borates of the fourth group members if the boric acid is present in small amounts. The group precipitate should not be allowed to stand exposed to the action of the air before filtration, as the alkaline solution will absorb CO_2, thus precipitating the carbonates of the fourth group.

Two methods are given for the analysis of this group.

Method I

The $(NH_4)_2S$ precipitate is thoroughly washed and divided into two portions, one small and one large.

A1—The small portion is heated with hot $HCl(1-1)$ a short time, and filtered if necessary. The filtrate is nearly neutralized with NaOH, 10 cc. of H_3PO_4 and 10 cc. of Na_2HPO_4 solutions added followed by 5 cc. of H_2O_2. A yellow coloration, not bleached by H_3PO_4, proves the presence of titanium.

A2—The large portion is transferred immediately to a beaker containing cold normal HCl (1 part of the dilute acid to 3 parts of water. Let stand about 5 minutes with occasional stirring. If a light colored residue remains, the HCl may be warmed to effect complete solution. Filter, wash with cold normal HCl. Treat the precipitate according to *B* and filtrate according to *C*.

OUTLINE OF GROUP ANALYSIS

A—The solution may contain cobalt, nickel, iron, aluminum, chromium, manganese, zinc and titanium.

Borates, fluorides, oxalates and tartrates are removed before the solution is made alkaline.

Add NH_4Cl, NH_4OH and $(NH_4)_2S$.

CoS, NiS, FeS, $Al(OH)_3$, $Cr(OH)_3$, $Ti(OH)_4$, MnS, ZnS.

Divide into two portions, one small and one large.
A1 Small portion.—H_2O_2 test for titanium.
A2 Large portion.—Treat with cold normal HCl.

B—CoS, NiS, black, $(Ti(OH)_4)$. Use H_2O_2+ NaHCO$_3$ or KNO$_2$ test for cobalt.	C—Filtrate: FeCl$_2$, AlCl$_3$, CrCl$_3$, ZnCl$_2$, MnCl$_2$, $(TiCl_4)$. Divide into two portions. Small portion—Add Cl water and make t● KCNS test for iron. Large portion—Oxidize the iron with Cl water, boil. Remove the phosphates if present. Add NH$_4$OH till alkaline. Filter.		
Use K C N test in KOH solution containing hypobromite or the KI test for nickel.	Basic acetates, hydroxides and phosphates of iron, chromium, a l u m i n u m , titanium a n d manganese. Divide into three portions: C1—H$_2$O$_2$ test for chromium. C2—Make alkali fusion and test water extraction w i t h NH$_4$Cl for aluminum. Cobalt nitrate ignition. C3—PbO$_2$ test for manganese.	D—Filtrate: ZnCl$_2 \cdot$2NH$_4$Cl, MnCl$_2 \cdot$2NH$_4$Cl. *If phosphates were not present:* Divide into two parts. $D1$—PbO$_2$ .test for manganese. $D2$—H$_2$S test for zinc. *If phosphates were present:* Divide into two small portions and one large one: D1—As above. D2—As above. D3—Large portion — Add NH$_4$OH and $(NH_4)_2$S. Filter.	
		ZnS, MnS. Discard.	E—Filtrate : May contain calcium, barium, strontium and magnesium. .Evaporate, add $(NH_4)_2CO_3$. Test filtrate and precipitate for group 4 elements.

B—Test with borax bead. A blue color of the bead indicates cobalt and brown indicates nickel, although it may be iron, inasmuch as large quantities of FeS dissolve in cold normal HCl slowly. Dissolve the sulphides in hot concentrated HCl, adding a few drops of concentrated HNO₃. If titanium is absent evaporate just to dryness and dissolve in 10 cc. of water.

If titanium has been found to be present it is likely to contaminate this solution and if so will interfere later. Consequently the solution is evaporated just to dryness, then diluted to about 50 cc., made just alkaline with a few drops of ammonia, boiled to coagulate the precipitate and filtered, discarding the precipitate. NaOH is added to the filtrate and solution boiled until the ammonia has been completely expelled, then the hydroxides of cobalt and nickel filtered off and dissolved in a minimum amount of HCl. The solution is evaporated just to dryness and dissolved in 10 cc. of water.

Use one of the following procedures:

1—Divide into two portions.

First Portion—Add an excess of KOH, precipitating Ni(OH)₂ and Co(OH)₂. Add Br water and boil until the hydroxides have turned black. Filter and wash the precipitate with water till the washings give no test for HBr with AgNO₃. Pour a hot solution of KI over the precipitate on the filter paper. Test the filtrate for the presence of free iodine with CS₂. A violet color proves the presence of *nickel*. (The KI solution must be fresh, as it must not contain free I.)

Second Portion—Add NaHCO₃ until effervescence ceases, then a few drops of H₂O₂, filter. A green colored filtrate proves the presence of cobalt.

2—Divide into two portions.

First Portion—Add 15 cc. of acetic acid, then 50 cc. of

KNO_2. Dilute to 100 cc. and let stand for an hour. A yellow precipitate indicates the presence of cobalt. Filter. Confirm by the borax bead test.

Second Portion—To the *neutral* solution add KCN, a few drops at a time, until any precipitate which forms at first just redissolves, then add *two drops* more. Boil for 2 or 3 minutes, filter off any residue that remains. Make a NaBrO solution by adding Br water to 50 cc. of NaOH until the solution has a deep yellow color. Pour the NaBrO solution into the filtrate. Allow to stand 10–15 minutes. Filter and test the precipitate with the borax bead. A black precipitate giving a red brown bead proves the presence of nickel. If this test is positive and considerable iron is found in the unknown confirm by the KI test.

C—The filtrate or solution resulting from the treatment with cold normal HCl is boiled until the H_2S is completely expelled and divided into one small portion and a large one.

Small Portion—Add a little chlorine water and evaporate to small bulk. Cool and add KCNS solution. A deep red solution proves the presence of *iron*.

Large Portion—If iron is present add a little chlorine water to oxidize the same and evaporate the excess of chlorine. The subsequent treatment depends on whether phosphates are present or not. If phosphates are not present the following paragraph may be omitted, but if present follow the details closely.

After cooling the solution add NH_4OH gradually with vigorous stirring until one drop of reagent gives a slight precipitate which just fails to redissolve. The solution should be acid. If alkaline make distinctly acid by the addition of a few drops of acetic. Add 5 cc. of $NH_4C_2H_3O_2$ (50% strength) and if a brownish red

color is not produced, add $FeCl_3$ solution drop by drop until such a red color develops. Add about 100 cc. of water, transferring the solution to a large vessel (a 250 cc. flask is convenient, because of the tendency of the solution to boil over) and boil for 2 or 3 minutes. Filter while hot, wash with hot water. Add 3–5 cc. more of $NH_4C_2H_3O_2$ to the filtrate, boil again as before and collect on a separate filter. Make filtrate just alkaline with NH_4OH. Boil until only a very slight odor of NH_4OH is perceptible. Filter. Unite precipitates. Save the filtrate for procedure D.

If phosphates are not present add 20 cc. of NH_4Cl solution and NH_4OH until just alkaline. Boil until the odor of NH_4OH is just barely perceptible. Filter. Wash with hot water. Test filtrate according to D.

The precipitate containing the basic acetates, hydroxides and phosphates or the hydroxides alone is divided into three portions.

$C1$—Transfer a little of the precipitate to an evaporator, add a few drops of $NaOH$ solution and H_2O_2. (Na_2O_2 may also be used for this reaction.) Boil until effervescence ceases, to insure complete oxidation and destroy the excess of H_2O_2. Dilute with 1 cc. of water and filter. A yellow filtrate indicates chromium. Add dilute H_2SO_4 drop by drop till just acid to litmus. Dilute with a little water and add a few drops of H_2O_2. A blue color proves the presence of *chromium.*

$C2$—Add an equal bulk of solid Na_2CO_3 to a small portion of the precipitate in a porcelain dish and add also half as much solid $Ba(OH)_2$. Boil with 5 cc. of water for two or three minutes, adding water to keep the volume constant. Filter into a test tube, rejecting the precipitate. To the filtrate add NH_4Cl solution and

boil for some time. A white flocculent precipitate proves the presence of *aluminum*.

C3—Dissolve in, HNO_3, add PbO_2, etc., testing as in *D1*. While manganese is not normally expected to precipitate with the iron, chromium, and aluminum, oxidation and occlusion combined frequently cause all of it to be precipitated with them, hence the test at this point is very essential if not affirmed in test *D1* previously.

D—The treatment in this division also depends on whether phosphates were originally present or not.

If phosphates were not present divide the filtrate into two parts.

D1—Boil under the hood with a few cc. of H_2SO_4 in an evaporating dish until the fumes of SO_3 appear, cool, transfer contents of the dish to a test tube half filled with HNO_3. Add PbO_2 in excess, heat to boiling and allow to settle or still better filter. A purple or red solution proves the presence of *manganese*.

D2—Make the second portion faintly acid with acetic, warm, pass H_2S into it. If no precipitate forms immediately allow to stand several minutes, as a small amount of ZnS precipitates slowly. A white precipitate, very soluble in HCl, proves the presence of zinc.

If phosphates were present divide the solution into two small parts and one large one.

D1—Test as above for manganese.

D2—Test as above for zinc.

D3—Evaporate to about 50 cc., add a few drops of NH_4OH to insure alkalinity, but avoiding an excess, then precipitate the zinc and manganese with $(NH_4)_2S$. Discard the precipitate. The filtrate may contain barium, strontium, calcium, and magnesium which were precipitated in this group because of the presence of phosphates. Evaporate to about 15 cc., add water if necessary to

redissolve any crystallized salts, add $(NH_4)_2CO_3$ and test precipitate and filtrate for the presence of the elements of Group IV.

Method II

A—The precipitated sulphides and hydroxides are dissolved in about 10 cc. of hot concentrated HCl, adding a drop or two of concentrated HNO_3 if necessary. Add an equal amount of water and filter if necessary.

B—Make solution alkaline with NaOH. If the solution forms a jelly, dilute somewhat. Cool and keep the solution cold (by immersing in cold water). Add about 3 gms. of Na_2O_2 *gradually*, a *very small portion* at a time, meanwhile stirring vigorously. Add 5 cc. of Na_2CO_3 solution, boil to decompose the excess of Na_2O_2. Dilute somewhat and filter. Test the filtrate according to *G*.

C—The precipitated hydroxides may also contain phosphates, and if so may contain members of Group IV as phosphates. The precipitate is dissolved in a minimum amount of hot concentrated HCl, forming the chlorides in solution. Dilute somewhat. If phosphates are present test for iron according to *C1* and remove the phosphoric acid by procedure *C2*. If they are not present follow *C3*.

C1—A small portion is tested for iron by adding KCNS solution. A deep blood-red solution proves the presence of *iron*.

C2—The large portion is neutralized by adding NH_4OH gradually with vigorous stirring until one drop of reagent gives a slight precipitate which just fails to dissolve. The solution should be acid. If alkaline make distinctly acid by the addition of a few drops of acetic acid. Add 5 cc. of $NH_4C_2H_3O_2$ (50% solution) and if a brownish red color is not produced, add $FeCl_3$ solution drop by drop until such a red color develops. Add about 100 cc.

Method II

OUTLINE OF GROUP ANALYSIS

A—The solution may contain cobalt, nickel, iron, aluminum, titanium, chromium, manganese and zinc.

Borates, fluorides, oxalates and tartrates are removed before the solution is made alkaline.

Add NH_4Cl, NH_4OH and $(NH_4)_2S$.

CoS, NiS, FeS, MnS, ZnS, $Al(OH)_3$, $Cr(OH)_3$, $Ti(OH)_4$.

Dissolve in hot concentrated HCl, adding a few drops of HNO_3 if necessary. Dilute, filter.

·*B*. $CoCl_2$, $NiCl_2$, $FeCl_2$ or $FeCl_3$, $MnCl_2$, $ZnCl_2$, $AlCl_3$, $CrCl_3$, $TiCl_4$.   Make alkaline with NaOH.   Add Na_2O_2.   Boil, filter.

C. Co, Ni, Fe, Mn, Ti hydroxides (or phosphates) with phosphates of Group IV. Dissolve in hot conc. HCl. *C1*. KCNS test for iron. *C2*. Remove phosphates if present. *C3*. Add NH_4Cl, then NH_4OH. Heat, stir, filter.	*G*. Na_3AlO_3, Na_2CrO_4, Na_2ZnO_2. Make acid with HNO_3, then alkaline with NH_4OH. Heat, filter.	
	G. $Al(OH)_3$, Cobalt nitrate ignition test for aluminum.	*H*. Filtrate: Na_2CrO_4, Na_2ZnO_2. Acidify with $HC_2H_3O_2$. Add $BaCl_2$. Filter.
D. Fe and Ti hydroxides or phosphates. Dissolve in hot HCl. Neutralize with NaOH. Add H_3PO_4, Na_2HPO_4, then H_2O_2 test for titanium.	*E*. Filtrate: $CoCl_2 \cdot 4NH_3$, $NiCl_2 \cdot 4NH_3$, $MnCl_2 \cdot 2NH_4Cl$. Add $(NH_4)_2S$. Filter. (Add filtrate to original group filtrate.) MnS, CoS, NiS. Treat with cold normal HCl.	*H*. $BaCrO_4$, yellow test for chromium. / *I*. Filtrate: $Zn(C_2H_3O_2)_2$ H_2S test for zinc.
	E1. CoS, NiS. Dissolve in HCl and a little HNO_3. *E2*. H_2O_2 + $NaHCO_3$ or KNO_2 test for cobalt. *E3*. KCN test in KOH solution containing hypobromite or the KI test for nickel.	*F*. $MnCl_2$. Boil off H_2S. Add NaOH. Filter. Dissolve residue in dilute HNO_3. PbO_2 test for manganese.

of water, transferring the solution to a large vessel (a 250 cc. flask is convenient, because of a tendency of the solution to boil over). Boil for 2 or 3 minutes. Filter while hot, wash with hot water. Add 3–5 cc. more of $NH_4C_2H_3O_2$ to the filtrate, boil again as before and collect on a separate filter. Proceed with $C3$.

$C3$—Add 10 cc. of NH_4Cl solution to filtrate and make just alkaline with NH_4OH. Heat to boiling. Filter. Unite precipitates for procedure D. Test filtrate according to E.

D—Dissolve in hot HCl. Neutralize with NaOH, leaving the solution just acid. Add 10 cc. of H_3PO_4, 10 cc. of Na_2HPO_4, then 5 cc. of 3% H_2O_2. A yellow to red coloration not bleached by H_3PO_4 proves the presence of titanium.

E—The cobalt, nickel and manganese are precipitated by $(NH_4)_2S$ in the filtrate, warming and stirring to coagulate the precipitate. Filter, wash with H_2S water. The filtrate may contain members of Group IV, hence is added to the original filtrate from the precipitation of this group of metals. Treat precipitate with cold normal HCl, allowing to stand about 5 minutes, add a little H_2S water, filter off the sulphides of cobalt and nickel from solution of $MnCl_2$. Test solution according to F.

$E1$—The sulphides are dissolved in a small amount of hot concentrated HCl, adding a few drops of concentrated HNO_3 if necessary, evaporate just to dryness and dissolve in 10 cc. of water. Use one of the following precedures:

Follow directions $B1$ or $B2$ of Method I.

F—Boil the H_2S from the filtrate. Add NaOH until just distinctly alkaline. Filter the manganese hydroxide and dissolve from filter in a small quantity of hot dilute HNO_3, catching filtrate in a test tube. Add about 2 gms. of PbO_2 (free from Mn), heat for a few minutes, allow to

settle. A violet red color proves the presence of manganese.

G—The filtrate from the Na_2O_2 treatment may contain Na_3AlO_3, Na_2CrO_4, Na_2ZnO_2. Make acid with concentrated HNO$_3$, then just decidedly alkaline with NH$_4$OH. Heat to coagulate precipitate and filter. Wash with hot water.

$G1$—A white precipitate indicates the presence of aluminum. It is dried, separated from paper, then ignited in a porcelain crucible. A drop or two of cobalt nitrate is added, then reignited. A blue color proves presence of aluminum.

H—The filtrate may contain Na_2CrO_4, yellow, and Na_2ZnO_2, colorless. Acidify with acetic acid and add $BaCl_2$ to complete precipitation if the solution is yellow; if not yellow proceed with I, as chromium is absent. Allow precipitate to settle, filter. A yellow precipitate of $BaCrO_4$ proves the presence of chromium. Test filtrate according to I.

I—Heat filtrate, pass H_2S until solution is saturated allowing to stand for 10 minutes if no precipitate forms at once. A white precipitate proves the presence of zinc.

GROUP IV

A—Evaporate the filtrate [1] from Group III to about 15 cc. If some of the salts have a tendency to crystal-

[1] In case of the absence of third group elements and phosphoric acid is present, this acid should be removed before evaporation by making the solution just acid with acetic, adding 5 cc. of a 50% solution of $NH_4C_2H_3O_2$ and FeCl$_3$ solution drop by drop until the red color of ferric acetate develops. 100 cc. of water is added and the solution boiled 2 or 3 minutes. Filter while hot. Add 3-5 cc. more of $NH_4C_2H_3O_2$ to filtrate and boil again. Filter, reject precipitates, after concentration add NH$_4$OH until the filtrate is alkaline, then $(NH_4)CO_3$ for the group precipitation,

lize out add just sufficient water to redissolve the same.
Sulphur usually deposits soon after boiling is com-
menced and should be filtered out, as it has a tendency
to interfere with future detections. This precipitate
should not be confused with a member of this group nor
should extreme dilution be attempted to dissolve this in-
soluble substance. Sometimes the CO_2 of the air will be
absorbed in sufficient quantity to precipitate the insol-
uble carbonates of this group. However, these are easily
dissolved in HCl if their formation is indicated. Add a
few drops of NH_4OH to insure alkalinity and $(NH_4)_2CO_3$
to complete precipitation. (Do not forget to add E of
Group III, if phosphates were present. If the addition
of NH_4OH above produces a precipitate it may be due
to phosphates which were present with an insufficient
amount of fourth group elements to cause their com-
plete precipitation, in which case they must be removed
by the ammonium acetate separation.) Warm the mix-
ture and let stand 10 minutes. Add a few more cc. of
$(NH_4)_2CO_3$ and filter immediately. Wash thoroughly
with water. Analyze the precipitate according to B
and filtrate according to D.

B—Heat about 5 cc. of $HC_2H_3O_2$ in a test tube and
pour this solution repeatedly through the filter. Wash
filter paper with a little warm water. The volume
should now be more than 10 cc. To a small portion add
K_2CrO_4. If no precipitate appears test the remainder of
the solution according to procedure C. If a precipitate
forms add K_2CrO_4 solution to the remainder to complete
precipitation, but avoiding a large excess. Warm gently,
filter. Wash the precipitate with a little water con-
taining acetic acid. Test the filtrate by C. $BaCrO_4$,
yellow, is precipitated, indicating the presence of barium.
Dissolve in HCl and divide into two portions.

Outline of Group Analysis

A—The solution may contain barium, strontium, calcium, magnesium, sodium, potassium and lithium.
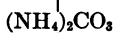
$$(NH_4)_2CO_3$$

B—BaCO₃, CaCO₃, SrCO₃, white. Dissolve in HC₂H₃O₂. Add K₂CrO₄. Filter.		*D*—MgCl₂·2NH₄Cl, KCl, NaCl, LiCl. Remove any of *B* with (NH₄)₂SO₄ and (NH₄)₂C₂O₄. Filter. Divide the filtrate into two portions.
BaCrO₄, yellow. *B1*—Use flame test. *B2*—Use sulphate test.	*C*—Filtrate.Acetates and chromates of calcium and strontium. Add NH₄OH and (NH₄)₂CO₃. Filter. Discard filtrate.	*D1*—U s e NaNH₄-HPO₄ test for magnesium. *D2* — Evaporate t o dryness. Heat to expel ammonium salts. Divide into two unequal parts.
	CaCO₃, SrCO₃, white. Dissolve in HC₂H₃O₂. Divide into two portions. *C1*—Use sulphate and flame tests for strontium. *C2*—Precipitate the strontium w i t h (NH₄)₂SO₄. Filter. Use the oxalate test for calcium confirming with the flame test.	Small part — Flame tests Large part—Dissolve in water, divide into three portions. *a*—Use Na₃Co(NO₂)₆ test for potassium. *b*—Use K₂H₂Sb₂O₇ test for sodium. *c*—Use Na₂HPO₄ test for lithium.

B1—Heat on a platinum wire.   A green flame proves the presence of *barium*.

B2—Add an equal volume of CaSO₄.   Let stand for 20 minutes if a precipitate does not form before that time.   A white crystalline precipitate, BaSO₄, insoluble in acids, proves the presence of *barium*.

[Barium may have been detected in Group II.]

C—Add NH₄OH till alkaline, then (NH₄)₂CO₃ to complete precipitation to free the calcium and strontium from the chromates and acetates.   Filter and wash the

precipitate until the yellow color of the wash water has entirely disappeared. Reject filtrate. Dissolve the carbonates in the smallest possible quantity of warm acetic acid. Divide into two portions.

C1—Add to one portion a small quantity of saturated $CaSO_4$ solution. Heat to boiling and allow to stand 30 minutes. A fine white precipitate, $SrSO_4$, indicates the presence of strontium. Filter, place the precipitate in a watch glass and add a drop of concentrated HCl. Make a flame test with the resulting solution. A deep red flame proves the presence of *strontium*.

C2—To the second portion add 10 cc. of a strong solution of $(NH_4)_2SO_4$. Boil a few minutes and filter. Wash the precipitate once with $(NH_4)_2SO_4$ solution. $SrSO_4$ is precipitated with some $CaSO_4$ by this treatment. Test the precipitate by the flame test. It should give the characteristic red flame. To the filtrate add NH_4OH till ammoniacal, heat to boiling and add $(NH_4)_2C_2O_4$ solution. Let stand 30 minutes if necessary. A white crystalline precipitate, CaC_2O_4, indicates the presence of *calcium*. Place the precipitate in a watch glass or in a small beaker, moisten with concentrated HCl and apply the flame test. If the precipitated oxalate is pure calcium oxalate the flame color will be yellow or orange, but not red. If red, strontium is present and should be removed by dissolving the oxalate in hot concentrated HCl and evaporating to dryness to decompose the oxalic acid. Dissolve in a little water, boil again with 10 cc. of $(NH_4)_2SO_4$ solution, filter, add $(NH_4)_2C_2O_4$, testing again as before.

D—To the filtrate from the $(NH_4)_2CO_3$ treatment add a few drops of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$, and allow to stand about 20 minutes. Filter if necessary. Reject the precipitate. Divide the filtrate into two portions. ·

D1—To one portion add NH_4OH and $NaNH_4HPO_4$. Let stand 30 minutes if necessary. If a flocculent precipitate forms dissolve it in the least amount of HCl necessary without filtration. Add NH_4OH, drop by drop, rubbing the inner surface of the test tube with a glass rod to facilitate precipitation. A white crystalline precipitate proves the presence of *magnesium*.

D2—Evaporate the second portion to dryness and ignite until all the ammonium salts are volatilized, i. e., until the white fumes cease to come off. It is very essential that the ammonium salts be completely expelled or they will interfere later. Divide into two unequal portions.

Small Portion—Moisten with HCl, introduce into the flame by means of a platinum wire. A *bright yellow* flame which masks the flame completely indicates the presence of sodium. Considerable care should be exercised in making this test, as the flame test is very delicate and this element is so widely distributed. Reagents frequently contain sodium and extreme care is hence necessary to avoid introducing this element preceding the test. A *violet* flame indicates the presence of potassium. The potassium flame is best seen when viewed through a blue glass. An *intense red* flame indicates lithium.

The flame should be examined with the aid of the spectroscope. See page 74.

Larger Portion—Dissolve in a little water. Divide into three parts.

a—Make one part slightly acid with acetic, add a few drops of $Na_3Co(NO_2)_6$, warm gently and allow to stand a few minutes. A yellow precipitate proves the presence of *potassium*.

b (see *b1*)—To another part add KOH, if necessary, drop by drop till the solution is neutral or slightly alkaline. Evaporate to 1 cc., cool. Add 1–2 cc. of $K_2H_2Sb_2O_7$ solu-

tion, pour into a test tube and let stand at least 30 minutes. A white crystalline precipitate (not flocculent) proves the presence of *sodium* in the absence of lithium. Confirmation with the flame test is a good policy.

b1—If lithium is indicated by flame color or spectroscopic examination it is removed by evaporation to 2–4 cc., addition of 1 cc. of strong NH_4OH and 2–4 cc. of 20 per cent. NH_4F solution. After standing a few minutes the precipitate is filtered out and tested for lithium by flame and spectroscopic tests. Add HCl to filtrate, evaporate to dryness. Dissolve in water and proceed as in *b*.

c—In the absence of magnesium, make alkaline with NaOH, evaporate to 2 or 3 cc. Filter off any precipitate. Add 1 cc. of Na_2HPO_4 solution. A white precipitate indicates the presence of lithium. Confirm by the spectroscope.

EXERCISE

1. What bases can be tested for directly in the original solution or solutions without interference from the others which may be present?

2. Why is dilute hydrochloric acid employed to precipitate the members of the first group of bases?

3. Why is it necessary to have a moderate excess of hydrochloric acid when the second group of bases is precipitated? Is a large excess of hydrochloric acid detrimental? Why?

4. Suppose that the arsenic was not completely dissolved in ammonium polysulphide in the group separation. Where would it interfere? Under the same conditions where would antimony and tin interfere?

5. Why is it necessary to pass hydrogen sulphide a second time to insure complete precipitation of the mem-

bers of Group II? If you obtain a moderately large precipitate, although precipitation is not complete, is it possible for you to miss any elements of this group? Explain.

6. If some of the hydrogen sulphide group members are left in solution will they interfere with future detections? Where will each member of the group interfere if left in solution due to incomplete precipitation with hydrogen sulphide?

7. What effect would be produced if you should accidently substitute ammonium polysulphide for ammonium monosulphide for the precipitation of the third group of bases?

8. Why is a large excess of ammonia detrimental in making the third group precipitation?

9. Suppose an indistinct test for manganese was obtained in Group III of the bases and the original substance dissolved in nitric acid giving a clear solution. How can you make a quick test for manganese?

10. Arsenic, magnesium, calcium and an obscure test for zinc were obtained in the analysis of the bases and hydrochloric, nitric and acetic acids were found in the acid analysis. Give a quick identification of zinc starting with the original material.

11. Suppose no precipitate forms when the group reagents of Group III of the bases are added and a phosphate was found to be present. How may the phosphate interfere in Group IV tests?

12. (a) What bases if incompletely removed in their respective groups will interfere with the magnesium test when it is applied? (b) What elements if incompletely removed in their proper group precipitations will be removed later by some group reagent preceding the magnesium test? Tabulate these elements showing where they are removed.

CHAPTER XVII

SHORT PROCESSES AND DEDUCTIONS

UNDER many conditions the processes of analysis may be made much shorter than the outlined procedure given in the previous chapter. While the student is making the analysis of an unknown the knowledge of the presence or absence of certain acids will frequently exclude certain bases by utilizing the solubility of the original unknown. This same principle is made use of continually throughout the analysis scheme for the acids especially in the second group. The student is urged to make as many deductive conclusions as possible. Being able to make good deductions will enable the student to eliminate many steps in the analysis of the bases and save many hours of hard mechanical labor in qualitative analysis. As a matter of suggestion and guide in the work the following list of solubilities is given:

The Metals, barium, strontium, calcium (slowly), lithium, sodium and potassium are soluble in water; silver, lead, mercury, bismuth, copper, cadmium, cobalt and nickel are slowly or not at all soluble in hydrochloric, but readily soluble in nitric, acid containing sufficient water to dissolve the product of reaction. Tin, manganese and zinc are soluble in very dilute nitric acid. Iron dissolves in hot moderately dilute nitric acid. The other metals are not soluble in nitric acid, but antimony dissolves readily in hydrochloric acid containing a little nitric to form aqua regia. Concentrated nitric acid converts antimony and tin into difficultly soluble antimonic

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and insoluble meta-stannic acids. The best solvent for aluminum, chromium, iron, manganese and zinc is hydrochloric acid. Free chlorine converts all the metals having soluble chlorides into a soluble form. Magnesium is soluble in all of the common inorganic acids.

(Consult the following table of solubilities for further information.)

The oxides and *hydroxides* of the alkalies, barium, strontium, are soluble in water; calcium oxide and the oxides of arsenic are sparingly soluble and the oxides of the other bases (if not acid-forming oxides, in which case they are detected among the acids and no conflict arises) are insoluble in water. All the common oxides are soluble in hydrochloric acid with the exception of chromous, chromic, ferric, aluminum, titanic, and stannic oxides, especially when strongly ignited, which are sparingly soluble in acids.

All Sulphides, except those of the alkalies and alkaline earths are insoluble in water.

All Ferrocyanides, except those of the alkalies, strontium, calcium and magnesium (of barium sparingly soluble), are insoluble in water. Chromium and arsenic form no compounds with the ferrocyanide.

Most Ferricyanides, except those of the alkaline earths and alkalies, are insoluble in water. Aluminum, antimony, chromium, ferric iron, lead, mercuric mercury, stannic tin and arsenic either form no compounds or compounds soluble in water.

The normal Cyanides of the alkalies, alkaline earths and mercuric mercury are soluble in water (barium cyanide being sparingly soluble). The other metallic cyanides are insoluble in water, but many double cyanides are soluble, including commonly those of zinc, nickel, silver, mercury, copper, cadmium, iron and cobalt.

TABLE OF SOLUBILITIES

	Ag	Pb	Hg (ous)	Hg (ic)	Bi	Cu	Cd	As	Sb	Sn (ous)	Sn. (ic)	Co	Ni
Metal.....	A	A	A	A	A	A	A	A	A	A	A	A	A
Oxide.....	A	A	A	A	A	A	A	A	A	A	A-I	A	A
Hydroxide	—	A	—	—	A	A	A	—	—	A	A	A	A
H₂S.......	A	A	A	A	A	A	A	A	A	A	A	A	A
H₄Fe(CN)₆	I	A	—	—	—	I	—	—	—	I	I	I	I
H₃Fe(CN)₆	I	W-A	—	—	—	—	—	—	—	I	—	I	I
HCN.....	I	A	—	W	—	A	A	—	—	—	—	A-I	A-I
HCNS....	I	A	A	A	—	A	W-A	—	—	—	W	W	W
HCl......	I	W-I	A-I	W	W-A	W	W	W	W-A	W	W	W	W
HBr......	I	W-I	A-I	W	W	W	W	W	W-A	—	—	W	W
HI.......	I	W-I	A	A	A	W	W	W	W-A	W	W	W	W
HIO₃.....	A	A	A	A	A	A	A	—	—	A	—	A	W-A
H₂CrO₄....	A	A-I	A	W-A	A	W	A	—	A	A	A-I	A	A
H₃AsO₄....	A	A	A	A	A	A	—	—	A	—	A	A	A
H₃AsO₃....	A	A	A	A	—	A	—	—	A	—	—	A	A
H₃PO₄....	A	A	A	A	A	A	A	A	W-A	A	A	A	A
H₂C₂O₄....	A	A	A	A	A	A	A	—	A	A	W	A	A
H₂SO₃.....	A	A	A	A	A	W-A	W-A	—	A	W-A	—	A	A
H₂SO₄.....	W-A	A-I	W-A	W	W	W	W	—	A	W	—	W	W
HClO₃....	W	W	W	W	W	W	W	—	—	W	—	W	W
HBrO₃....	W-A	W	W	W	W	W	W	—	—	—	W	W	W
H₃BO₂....	A	A	—	—	A	A	W-A	—	—	A	—	A	A
H₂C₄H₄O₆..	A	A	W-A	A	A	W	W-A	—	A	A	—	W	A
HC₂H₃O₂..	W	W	W-A	W	W	W	W	—	—	W	W	W	W
HNO₃.....	W	W	W	W	W	W	W	—	—	—	—	W	W
H₂CO₃....	A	A	A	A	A	A	A	—	—	—	—	A	A
H₂SiO₃....	—	A	A	—	—	A	A	—	—	—	—	A	A
HF.......	W	A	—	W-A	W	A	W-A	W	W	W	W	W-A	W-A

W =Soluble in water.
W-A =Slightly soluble in water; readily soluble in acids.
A =Insoluble in water; soluble in acids.
W-I =Slightly soluble in water; slightly soluble in acids.

All Chlorides, Bromides and *Iodides*, with the exception of those of silver, lead, cuprous copper, mercurous mercury, and HgI₂, are soluble in water.

TABLE OF SOLUBILITIES

Fe (ous)	Fe (ic)	Cr	Al	Ti	Mn	Zn	Ba	Sr	Ca	Mg	Na	K	NH₄	Li
A	A	A	A	A	A	A	W	W	W	A	W	W	—	W
A	A	A-I	A	A	A	A	W	W	W-A	A	W	W	—	W
A	A	A	A	A	A	A	W	W	W-A	A	W	W	W	W
A	A	A-I	A	A	A	A	W	W	W-A	A	W	W	W	W
I	I	—	—	—	A	A-I	W-A	W	W	W	W	W	W	W
I	W	—	—	—	I	A	—	—	W	W	W	W	W	W
A-I	—	A	—	—	A	A	W-A	W	W	W	W	W	W	—
W	W	W	—	—	W	W	W	W	W	W	W	W	W	W
W	W	W-I	W	W-A	W	W	W	W	W	W	W	W	W	W
W	W	W-I	W	W-A	W	W	W	W	W	W	W	W	W	W
W	W	W	W	—	W	W	W	W	W	W	W	W	W	W
A	A	A	W-A	—	W-A	A	A	W-A	W-A	W-A	W	W	W	W
—	W	A-I	A	—	W	W	A	W-A	W	W	W	W	W	W
A	A	A	A	A	A	A	A	A	A	A	W	W	W	W-A
A	A	—	—	A	A	—	A	A	A	A	W	W	W	W-A
A	A	A	A	A	A	A	A	A	A	A	W	W	W	W-A
A	A	W-A	A	—	W-A	A	A	A	A	A	W	W	W	W
W	W	W-I	W	W-A	W	W	I	I	W-I	W	W	W	W	W
W	W	W	W	—	W	W	W	W	W	W	W	W	W	W
W	W	W	W	—	W	W	W	W-A	W	W	W	W	W	W
A	A	A	A	—	A	A	A	A	A	W-A	W	W	W	W
W-A	W	W	W	—	W-A	A	A	A	A	W-A	W	W	W	W
W	W	W	W	A	W	W	W	W	W	W	W	W	W	W
W	W	W	W	—	W	W	W	W	W	W	W	W	W	W
A	—	—	—	—	A	A	A	A	A	A	W	W	W	W-A
A	A	A	A-I	—	A	A	A	A	A	A	W	W	—	W
W-A	W	W	W	W	A	W-A	W-A	W-A	A-I	W-A	W	W	W	W-A

A-I = Insoluble in water; slightly soluble in acids.
 I = Insoluble in both water and acids.
 — = Solubility unknown.

The iodates of the alkalies only are soluble in water. The insoluble iodates are transposed by strong acids with (HI) or without (H₂SO₄, HNO₃, HCl) decomposition of the iodic acid.

The Chromates of the alkalies, magnesium, copper, zinc and calcium are soluble; of mercuric mercury and strontium slightly soluble; of barium, manganese, bismuth, mercurous mercury, silver and lead insoluble in water.

All Arsenates, except those of the alkalies and alkaline earths, are insoluble in water, but soluble in acids.

All Arsenites, except those of the alkalies, are insoluble in water, but soluble in acids.

All Phosphates, except those of the alkalies (lithium sparingly), are insoluble in water, but are either transposed or dissolved by HNO_3, H_2SO_4 or HCl. All are dissolved in $HC_2H_3O_2$ except those of lead, aluminum, bismuth and ferric iron.

All Oxalates, except those of the alkalies, stannic tin, manganese and chromium are insoluble in water. The metallic oxalates are transposed by HCl, HNO_3 and H_2SO_4, and solution is effected when the corresponding chlorides, nitrates and sulphates are soluble.

All normal Sulphites, except those of the alkalies, are insoluble in water, decomposed by all mineral acids. (Sulphites oxidize readily to sulphates, then give reactions of the latter salts.)

All Sulphates are soluble in water except those of barium, strontium, lead, mercurous mercury and calcium.   ($CaSO_4$ and Hg_2SO_4 are slightly soluble.)

All Nitrates, Acetates and *Chlorates* are soluble in water.

All Bromates are soluble in water, silver and barium bromates being the least soluble (1 part in 120 at 20°). The bromates are transposed by strong acids with slow (H_2SO_4, HNO_3) or rapid (HCl, HBr), decomposition of the bromic acid.

All Carbonates and *Borates*, except those of the alkalies, are insoluble in water, but readily soluble in dilute acids.

The Tartrates of the alkalies are soluble in water; potassium and ammonium acid tartrates are sparingly soluble. Tartrates of non-alkaline bases and alkaline earth bases are insoluble or sparingly soluble. Some double tartrates, as $KSbOC_4H_4O_6$, are soluble in water. HCl, HNO_3 and H_2SO_4 transpose the tartrates.

All Nitrites are soluble in water, but silver nitrite and potassium and ammonium cobaltic nitrites are sparingly soluble.

The Silicates of sodium and potassium are soluble in water. All others are insoluble in water but soluble in acids with the exception of the silicate of aluminum, which is soluble with difficulty in acids. The solubility of silicates as listed above will not apply to the natural silicates, which are for the most part insoluble in water and acids, but soluble in acids after fusion with Na_2CO_3 provided the bases present form soluble salts with the acid employed. The solubility of the silicates in acid is due to transposition of the silicates forming soluble salts of the metals and hydrosol silicic acid.

The fluorides of the alkalies, aluminum, titanium, chromium, ferric iron, silver, bismuth, and stannic tin are soluble in water. The other fluorides are soluble with difficulty or insoluble in water but soluble in acids with the exception of the fluorides of calcium and magnesium, which are difficultly soluble in acids. The solubility in acids is due to transposition.

Suppose that an unknown dissolved in water, and phosphoric acid was the only acid found. Your conclusion is that only the alkalies can be present. No

other bases need be tested for because phosphates of the other bases are insoluble in water and if they were present the material would not have dissolved completely in water. Again, suppose that a sulphate and an iodide were found to be present and that the substance dissolved readily in dilute HNO_3. Silver, lead, mercury, barium, strontium and calcium are absent and need not be tested for because these elements form salts with the sulphate or iodide which are insoluble in HNO_3. Still again, suppose a chromate and a ferrocyanide are found in the acid analysis. Only the alkalies can be present if the original substance dissolved in water. If nitrates and acetates only were found in the acid analysis, all the bases may be present. Many other examples might be given. The student can usually eliminate certain of the bases, sometimes most of them, by this kind of reasoning after the acid analysis of each unknown.

If the unknown is a solution, test it with litmus and note if acid or alkaline. If acid or alkaline neutralize with an alkali or acid. If no precipitate forms then the deductions based on these solubilities are still good. If a precipitate forms, often good indications can be obtained by testing its solubility.

Making use of differential solubility of an unknown substance in various solvents, aqueous and non-aqueous, and analysis of each resulting solution for the basic and acid constituents will frequently give information regarding the particular acid in combination with a certain base and vice versa. Sometimes this method of ascertaining the exact molecular compounds is very simple, but usually the process is more or less complex and somewhat difficult for a course in elementary qualitative work. However, the student should draw conclusions

regarding the constitution of the compound or compounds in question whenever possible, utilizing all the information available for the purpose.

Suppose in the process of analysis the unknown substance dissolved in water and the solution was neutral. A chloride and sulphate were found to be the acids present and potassium was the only base. The original compounds were potassium sulphate and potassium chloride. If the solution was found to be acid an acid sulphate was probably present. If the substance was not a solid but a solution instead and that solution was acid, then free hydrochloric acid or sulphuric acid might have been added in making the solution.

Again, suppose the unknown partially dissolved in water and the remainder in hydrochloric acid. In the water extraction ammonia and a sulphate were found. In the acid extraction barium was the only base detected and a test for carbonate was found with the original substance. Your conclusion is that you had been given a mixture of ammonium sulphate and barium carbonate.

During the treatment of an unknown with the usual solvents hydrochloric acid was found to dissolve the substance completely with the evolution of a gas which was identified as hydrogen. The substance had a metallic lustre and was attracted by a magnet. Iron was the only base found with no acids. Your conclusion is naturally that your unknown was metallic iron.

After each complete analysis consult the solubilities of the substances and draw all possible conclusions regarding the composition of the original substance.

1. What bases might be present in an unknown that was not soluble in water but dissolved in dilute hydrochloric acid, giving a colorless solution? The acids carbonic and oxalic were found to be present.

2. Suppose you find the acids hydrochloric, hydriodic, chromic and sulphuric and the bases sodium, chromium, potassium, with a doubtful test for barium. The original material dissolved in water. What is your conclusion in regard to the barium test? Why?

3. What bases may be eliminated under the following conditions? The original solid is white and not soluble in water but completely soluble in hot dilute hydrochloric acid. No acids are found.

4. What acids can not be present in an absolutely colorless or white solid?

5. Are there any bases which can not be present in a colorless solid? If so, name them.

6. The original solid is black. No acids are found. How many possibilities have you in the analysis of the bases?

7. The solid dissolved in nitric acid, giving a yellow globule of semi-solid material, which floated on top of the solution. What is indicated?

8. An unknown was white and dissolved completely in considerable water and easily in sodium carbonate. Arsenous acid and no bases were found by analysis. What was the original substance? How many bases should have been tested for on the basis of the acid analysis?

9. A sulphide is found to be present. The original solid dissolves in water, giving an alkaline solution. How many bases can be present?

10. A white unknown was insoluble in water and acids. By fusing with Na_2CO_3 and extracting the fusion with water an insoluble residue remained. The water extraction gave a test for sulphate. What does this indicate the residue to contain?

11. An unknown is homogeneous and yellow in color. It dissolves slowly in hot hydrochloric acid, and on cooling, white needle-like crystals separate, leaving a yellow solution. What is indicated?

12. An unknown consists of glittering steel gray material soluble in hydrochloric acid and in nitric acid. With the first-named acid a gas is evolved which gives a miniature explosion when a lighted match is placed at the mouth of the test tube. What is indicated?

13. An unknown is almost black and is attracted by a magnet. What conclusion can be drawn?

14. Tartaric acid and boric acid were found to be present in an unknown, which was easily soluble in water. What bases need be tested for?

15. A white solid dissolves rather slowly in water with the evolution of heat. No acids are present. What conclusion is warranted?

16. Hydrochloric acid was the only acid found to be present. The unknown was insoluble in water and the acids, but soluble in ammonium hydroxide. What compound is indicated? How can you prove your conclusion?

17. An unknown solution gives the characteristic odor of acetic acid. Nitrous acid was the only other acid found and cobalt the only base detected preceding the ammonium carbonate group. How many of the alkalies need be tested for? Is it possible to find ammonia present?

18. An iodate is known to be present in a white solid which is readily soluble in water. What bases and acids

are eliminated? If acidified with sulphuric acid it gives no coloration, what others are eliminated?

19. What elements would ordinarily be analyzed for in (a) a metallic wire, (b) a brittle metallic ribbon, (c) a malleable metallic solid, (d) a brittle metallic solid?

20. A sulphide has been found in a solution which is strongly alkaline. What bases are eliminated?

LIST OF REAGENTS

Acids

Acetic, $HC_2H_3O_2$, 4N. 240 cc. of glacial acetic per liter.

Boric, H_3BO_3, a saturated solution.

Hydrochloric, HCl, concentrated, sp. gr. 1.20, 13N.

Hydrochloric, HCl, dilute, 3N. 230 cc. of the acid sp. gr. 1.20 per liter.

Hydrochlorplatinic, H_2PtCl_6, 0.5N. 10.3 gm. for each 100 cc.[2] Made by diluting the strong acid the appropriate amount or by dissolving 4.9 gm. of platinum as follows: The clean platinum is covered with concentrated hydrochloric acid and nitric acid added a *very small portion* at a time with gentle heating on a water bath until solution is effected. Any small black residue is filtered out. The solution is evaporated to syrupy consistency, then dissolved in water and diluted to 100 cc.

Hydrofluoric, HF, 40% solution (paraffin bottle).

Nitric, HNO_3, concentrated, sp. gr. 1.42, 16N.

Nitric, HNO_3, dilute, 6N. 260 cc. of the acid, sp. gr. 1.42, per liter.

Sulphuric, H_2SO_4, concentrated, sp. gr. 1.84, 36N.

Sulphuric, H_2SO_4, dilute, 9N. 250 cc. of the acid, sp. gr. 1.84, per liter.

Tartaric, $H_2C_4H_4O_6$, 2N. 150 gm. per liter.

Alkalies

Ammonium hydroxide, NH_4OH, concentrated, sp. gr. 0.90, 15N.

Ammonium hydroxide, NH_4OH, dilute, 5N.   330 cc. of the alkali sp. gr. 0.90 per liter.

Calcium hydroxide, $Ca(OH)_2$, lime-water.   A saturated solution.

Potassium hydroxide, KOH, 2N.   (The solid contains about 20% water.)   140 gm. per liter.

Sodium hydroxide, NaOH, 4N.   (The solid usually contains about 10% water.)   178 gm. per liter.

Sodium hydroxide, NaOH, 10%.   110 gm. per liter.

Miscellaneous Solutions and Liquids

Alcohol, ethyl, C_2H_5OH.

Aluminum sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$, 0.25N.   26 gm. per liter.[6]

Ammonium acetate, $NH_4C_2H_3O_2$, 50% solution, 6.5N. 500 gm. per liter.

Ammonium carbonate, $(NH_4)_2CO_3$, 4N.   Dissolve 195 gm. of the salt in a mixture of 80 cc. of concentrated NH_4OH and 500 cc. of water without heating.   Dilute to a liter.

Ammonium chloride, NH_4Cl, 2N.   107 gm. per liter.

Ammonium fluoride, NH_4F, 20% solution.   200 gm. per liter.

Ammonium molybdate, $(NH_4)_2MoO_4$.   Dissolve 100 gm. of MoO_3 in a mixture of 80 cc. of NH_4OH (sp. gr. 0.90) and 400 cc. of cold water.   Allow to cool and pour with constant stirring slowly into 400 cc. of HNO_3 (sp. gr. 1.42) and 600 cc. of water, keeping the solution cool or MoO_3 will precipitate.   Allow to stand at least 24 hours.   Decant and use the clear solution.

Ammonium oxalate, $(NH_4)_2C_2O_4$.   A saturated solution.

Ammonium monosulphide (colorless), $(NH_4)_2S$.   Pass H_2S into a concentrated solution of NH_4OH until the

solution is saturated, add an equal volume of concentrated NH_4OH and dilute with three volumes of water.

Note: The superscript figures are used to designate the number of hydrogen equivalents utilized to compute the number of grams of substance per liter of solution. Thus, 26 gm. per liter.[6] The six represents the number by which the molecular weight was divided to obtain the number of grams to be dissolved for a normal solution. A star signifies that the computation is made on the basis of the oxidizing equivalent. In all other cases the normalities of the solutions are computed with respect to the equivalent capacities of the substances to form salts.

Considering such a salt as $NaNH_4HPO_4$ the hydrogen equivalent is considered three from the capacity of PO_4 to unite with bases even though all the hydrogens have not been replaced by base.

Ammonium polysulphide (yellow), $(NH_4)_2S_x$. Proceed as with the monosulphide, but before diluting add about a gram of flowers of sulphur per liter of solution. After solution of the sulphur dilute with an equal volume of water.

Antimony trichloride, $SbCl_3$. 25 gm. of substance, 250 cc. of concentrated HCl, dilute to a liter.

Antimony pentachloride, $SbCl_5$. 30 gm. of substance, 250 cc. of concentrated HCl, dilute to a liter.

Barium chloride, $BaCl_2 \cdot 2H_2O$, N. 122 gm. per liter.[2]

Bismuth chloride, $BiCl_3$, 0.25N. 26 gm. per liter.[3] (Or use 40 gm. of $Bi(NO_3)_3 \cdot 5H_2O$ per liter.) Sufficient mineral acid must be present to prevent hydrolysis.

Bromine water, Br_2. A saturated solution.

Cadmium chloride, $CdCl_2 \cdot 2H_2O$, 0.5N. 55 gm. per liter.[2]

Calcium chloride, $CaCl_2$, N. 56 gm. per liter.[2]

Calcium sulphate, $CaSO_4$.   A saturated solution.

Carbon bisulphide, CS_2.

Chlorine water, Cl_2.   A saturated solution.   The solution decomposes less readily if kept in a dark place or in a bottle of dark colored glass.

Chromium sulphate, $Cr_2(SO_4)_3$, 0.5N.   33 gm. per liter.[6]

Cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, 0.25 N.   36 gm. per liter[2] (or 32 gm. of $CoSO_4 \cdot 7H_2O$ per liter).

Copper ammonia solution, $CuSO_4 \cdot 4NH_3$.   1.5 gm. of $CuSO_4 \cdot 5H_2O$ dissolved in water, an excess of ammonia added and diluted to a liter.

Copper sulphate, $CuSO_4 \cdot 5H_2O$, 0.5N.   63 gm. per liter.[2]

Ferric chloride, $FeCl_3 \cdot 6H_2O$, N.   91 gm. per liter.[3]

Ferrous sulphate, $FeSO_4 \cdot 7H_2O$.   Dissolve 150 gm. of the crystallized salt per liter of water, add a few clean scraps of iron or iron tacks and 5 cc. of concentrated H_2SO_4.   A cork stopper is employed.

Hydrogen peroxide, H_2O_2, 3% solution.

Indigo solution.   Place five parts of fuming sulphuric acid in a beaker immersed in cold water.   Add slowly with constant stirring one part of finely pulverized indigo.   Allow the covered beaker to stand two days.   Pour into twenty times its volume of water, stir thoroughly, filter.

Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, N.   190 gm. per liter.[2]   A little free acetic acid should be added to keep the solution clear.

Lithium chloride, $LiCl$, 0.1N.   4.3 gm. per liter.[1]

Magnesium sulphate, $MgSO_4 \cdot 7H_2O$, 0.5N.   61.5 gm. per liter.[2]

Magnesia mixture, $MgCl_2$, NH_4Cl, NH_4OH.   Dissolve 100 gm. of crystallized magnesium chloride and 200 gm. of ammonium chloride in 1300 cc. of water, then dilute

to two liters with dilute ammonium hydroxide (sp. gr. 0.96.)

Manganese sulphate, $MnSO_4 \cdot 4H_2O$, 0.5N.   56 gm. per liter.[2]   60 gm. of $MnSO_4 \cdot 5H_2O$ or 69 gm. of $MnSO_4.7H_2O$ can be used.)

Mercuric chloride, $HgCl_2$.   A saturated solution.

Mercurous nitrate, $HgNO_3 \cdot H_2O$, 0.25N.   70 gm. per liter.[1]

Nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, 0.25N.   36 gm. per liter.[2]   Or 32 gm. of $NiSO_4 \cdot 7H_2O$ per liter.[2]

Potassium acid pyro-antimonate, $K_2H_2Sb_2O_7$, 0.2N. Add 21.6 gm.[4] of solid to somewhat less than a liter of boiling water, boil for a minute until nearly all the salt is dissolved, quickly cool the solution, add about 30 cc. of 10% KOH and filter.   Dilute to a liter.   If a flocculent precipitate settles out on standing decant off the clear solution.   It should be tested frequently with a known solution of sodium salt.

Potassium bromate, $KBrO_3$, 0.2N.   5.6 gm per liter.[6*]

Potassium bromide, KBr, 0.2N.   20 gm. per liter.[1]

Potassium chlorate, $KClO_3$, 0.2N.   4.1 gm. per liter.[6*]

Potassium chloride, KCl, 0.5N.   37 gm. per liter.[1]

Potassium chromate, K_2CrO_4, N.   97 gm. per liter.[2]

Potassium cyanide, KCN, 0.5N.   33 gm. per liter.[1]

Potassium dichromate, $K_2Cr_2O_7$, N.   49 gm. per liter.[6*]

Potassium ferricyanide, $K_3Fe(CN)_6$, N.   110 gm. per liter.[3]

Potassium ferrocyanide, $K_4Fe(CN)_6$, N.   106 gm. per liter.[4]

Potassium iodate, KIO_3, 0.2N.   7.2 gm. per liter.[6*]

Potassium iodide, KI, 0.2N.   33 gm. per liter.[1]

Potassium nitrite, KNO_2, 50% solution.   500 gm. per liter.

Potassium nitrite, KNO_2, N.   85 gm. per liter.[1]

Potassium permanganate, $KMnO_4$, 0.1N. 3.2 gm. per liter.[5] *

Potassium sulphide, K_2S, 0.2N. 11 gm. per liter.[2]

Potassium sulphate, K_2SO_4, 0.5N. 44 gm. per liter.[2]

Potassium sulphocyanate, KCNS, N. 97 gm. per liter.[1]

Silver ammonia solution, $AgNO_3 \cdot NH_3 + NH_4OH$. 20 gm. of $AgNO_3$ and 32 gm. of NH_3 per liter.

Silver nitrate, $AgNO_3$, 0.5N. 85 gm. per liter.[1]

Silver sulphate, Ag_2SO_4. A saturated solution.

Sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$, N. 136 gm. per liter.[1]

Sodium ammonium phosphate, $NaNH_4HPO_4 \cdot 4H_2O$, 0.3N. 63 gm. per liter.[3]

Sodium arsenate, $Na_2HAsO_4 \cdot 7H_2O$, N. 104 gm. per liter.[3]

Sodium arsenite, $NaAsO_2$, 0.5N. 65 gm. per liter.[1]

Sodium borate, borax, $Na_2B_4O_7 \cdot 10H_2O$, 0.5 N. 96 gm. per liter.[2]

Sodium carbonate, Na_2CO_3. A saturated solution.

Sodium carbonate, Na_2CO_3, 5%. 50 gm. of anhydrous salt or 136 gm. of $Na_2CO_3 \cdot 10H_2O$ per liter.

Sodium chloride, NaCl, 0.5N. 29 gm. per liter.[1]

Sodium cobaltic nitrite, $Co(NO_2)_3 \cdot 3NaNO_2$. 100 gm. of sodium nitrite are dissolved in 300 cc. of water, acetic acid added to give slight acid reaction, then 10 gm. of cobalt nitrate. After standing several hours the solution is filtered if necessary. The solution has a tendency to decompose, consequently only small quantities should be prepared at a time.

Sodium nitrate, $NaNO_3$, N. 85 gm. per liter.[1]

Sodium oxalate, $Na_2C_2O_4$, 0.5N. 34 gm. per liter.[2]

Sodium phosphate, $Na_2HPO_4.12H_2O$, 0.3N. 119 gm. per liter.[3]

Sodium sulphite, $Na_2SO_3 \cdot 7H_2O$, 0.5N. 63 gm. per liter.[2]

Sodium tartrate, $Na_2C_4H_4O_6 \cdot 2H_2O$. 0.5N. 58 gm. per liter.[2]

Stannic chloride, $SnCl_4$, 0.5N. 33 gm. per liter.[4]

Stannous chloride, $SnCl_2 \cdot 2H_2O$. Dissolve 100 gm. of crystallized salt in 200 cc. of concentrated HCl and dilute to a liter. Or dissolve 55 gm. of metallic tin in 225 cc. of concentrated HCl and dilute to a liter. A few granules of metallic tin should be kept in the bottle. Use a cork stopper.

Strontium chloride, $SrCl_2 \cdot 6H_2O$, 0.5N. 67 gm. per liter.[2]

Titanium sulphate, $Ti(SO_4)_2$, 0.2N. Fuse 5.6 gm. TiO_2 with about 25 gm. of previously fused potassium bisulphate to a dead roast in a platinum dish, then add 25 gm. more of the bisulphate and fuse again. Extract the fusion when *cold* with *cold* 10% H_2SO_4. If the fusion melt does not all dissolve fuse again and re-extract. Dilute with cold 10% H_2SO_4 to a liter.[4]

(K_2TiF_6 can be dissolved in water treated with sulphuric acid and evaporated to SO_3 fumes to remove the HF and diluted with 10% sulphuric acid as above.)

Zinc sulphate, $ZnSO_4 \cdot 7H_2O$, 0.5N. 67 gm. per liter.[2]

Solid Reagents

Aluminum turnings.
Ammonium chloride, NH_4Cl.
Ammonium nitrate, NH_4NO_3.
Ammonium sulphate, $(NH_4)_2SO_4$.
Borax, $Na_2B_4O_7 \cdot 10H_2O$.
Calcium fluoride, CaF_2 (free from SiO_2).
Charcoal sticks, for blowpipe work.

Copper foil.
Cotton, absorbent.
Ferrous sulphate, $FeSO_4 \cdot 7H_2O$.
Iron (nails or tacks free from As, Sb and Sn).
Lead dioxide, PbO_2 (Manganese free).
Litmus paper.
Potassium acid sulphate, $KHSO_4$.
Potassium bromate, $KBrO_3$.
Potassium chlorate, $KClO_3$.
Potassium hydroxide, KOH.
Potassium iodate, KIO_3.
Potassium persulphate $K_2S_2O_8$.
Silica, SiO_2.
Silver nitrate, $AgNO_3$.
Sodium chloride, $NaCl$.
Sodium carbonate, Na_2CO_3.
Sodium hydroxide, $NaOH$.
Sodium peroxide, Na_2O_2.
Sodium and potassium carbonates, $Na_2CO_3 + K_2CO_3$.
Sodium sulphite, $Na_2SO_3 \cdot 7H_2O$.
Tin, granulated.
Turmeric paper.
Zinc, granulated.

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